



AGRICULTURAL RESEARCH INSTITUTE

PUSA







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OF  
NEW SOUTH WALES

FOR  
1936.  
(INCORPORATED 1881)

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Parts I and II

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NOTICE.

THE ROYAL SOCIETY of New South Wales originated in 1821 as the "Philosophical Society of Australasia"; after an interval of inactivity, it was resuscitated in 1850, under the name of the "Australian Philosophical Society", by which title it was known until 1856, when the name was changed to the "Philosophical Society of New South Wales"; in 1866, by the sanction of Her Most Gracious Majesty Queen Victoria, it assumed its present title, and was incorporated by Act of the Parliament of New South Wales in 1881.

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Authors should submit their papers in typescript and in a condition ready for printing. All physico-chemical symbols and mathematical formulæ should be so clearly written that the compositor should find no difficulty in reading the manuscript. Sectional headings and tabular matter should not be underlined. Pen-illustrations accompanying papers should be made with black Indian ink upon smooth white Bristol board. Lettering and numbers should be such that, when the illustration or graph is reduced to  $3\frac{1}{2}$  inches in width, the lettering will be quite legible. On graphs and text figures any lettering may be lightly inserted in pencil. Photomicrographs should be rectangular rather than circular, to obviate too great a reduction. The size of a full page plate in the Journal is  $4 \times 6\frac{1}{2}$  inches, and the general reduction of illustrations to this limit should be considered by authors. When drawings, etc., are submitted in a state unsuitable for reproduction, the cost of the preparation of such drawings for the process-block maker must be borne by the author. The cost of colouring plates or maps must also be borne by the author.

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[Those persons who feel disposed to benefit the Royal Society of New South Wales by Legacies, are recommended to instruct their Solicitors to adopt the above Form of Bequest.]

# PUBLICATIONS.

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Transactions of the Philosophical Society, N.S.W., 1862-5, pp. 374, out of print.

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| 1898 |      | Alexander, Frank Lee, Surveyor, 21 George-street, Parramatta; p.r. 154 William-street, Granville.   |
| 1905 | P 3  | Anderson, Charles, M.A., D.Sc. ( <i>Edin.</i> ), C.M.Z.S., Director of the Australian Museum, College-street, Sydney; p.r. 17 Towns-road, Vaucluse. (Hon. Secretary.) (President, 1924.)                  |
| 1909 | P 10 | Andrews, Ernest C., B.A., Hon. Mem. Washington Academy of Sciences and of Royal Society of New Zealand, No. 4, "Kuring-gai," 241 Old South Head-road, Bondi. (President, 1921.)                           |
| 1933 |      | Andrews, John, B.A., Ph.D., Lecturer in Geography in the University of Sydney; p.r. 20 Woolwich-road, Hunter's Hill.  |
| 1935 |      | Ash, Percy Arthur, D.D.S., University Lecturer, 135 Macquarie-street, Sydney.   |
| 1930 |      | Aston, Ronald Leslie, B.Sc., B.E. <i>Syd.</i> , M.Sc., Ph.D., <i>Cantab.</i> , A.M.I.E.Aust., Lecturer in Civil Engineering and Surveying in the University of Sydney; p.r. 24 Redmyre-road, Strathfield. |
| 1919 |      | Aurousseau, Marcel, B.Sc., "Dirrilong," 54 Park View-road, Manly.   |
| 1935 |      | Back, Catherine Dorothy Jean, M.Sc., The Women's College, Newtown.  |
| 1878 |      | Backhouse, His Honour Judge A. P., M.A., "Melita," Elizabeth Bay.   |
| 1924 | P 1  | Bailey, Victor Albert, M.A., D.Phil., F.Inst.P., Assoc.-Professor of Physics in the University of Sydney; p.r. 12 Cranbrook-avenue, Cremorne.   |
| 1919 |      | Baker, Henry Herbert, F.S.M.C., c/o W. Watson & Son Ltd. Watson House, Bligh-street, Sydney; p.r. 18 Bradley's Head-road, Mosman.   |
| 1894 | P 28 | Baker, Richard Thomas, The Crescent, Cheltenham.  |

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| 1895 | P 9  | Barraclough, Sir Henry, K.B.E., B.E., M.M.E., M.Inst.C.E., M.I.Mech.E., Memb. Soc. Promotion Eng. Education; Memb. Internat. Assoc. Testing Materials; Professor of Mechanical Engineering in the University of Sydney. |
| 1935 |      | Bayley, Arthur, 6 Martin-road, Centennial Park.   |
| 1933 |      | Bedwell, Arthur Johnson, Eucalyptus Oil Merchant, "Kama," 10 Darling Point-road, Edgecliff.   |
| 1926 |      | Bentivoglio, Sydney Ernest, B.Sc.Agr., c/o Tooth & Co. Limited, Sydney; p.r. 52 Crows Nest Road, North Sydney.  |
| 1923 |      | Birks, George Frederick, Wholesale Druggist, c/o Potter & Birks Ltd., 15 Grosvenor-street, Sydney; p.r. 42 Powell-street, Killara.  |
| 1916 |      | Birrell, Septimus, 74 Edinburgh-road, Marrickville.   |
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| 1933 |      | Boan, Robert Farquharson, A.A.C.I., Analyst and Consulting Chemist, 185 Elizabeth-street, Sydney.   |
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| 1932 |      | Boon, Herbert Eril, 10 Murdoch-street, Cremorne.  |
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| 1922 |      | Bradfield, John Job Crew, O.M.G., D.Sc. Eng., M.E., M.Inst.C.E., M.Inst.E.Aust., Barrack House, 16 Barrack-street, Sydney; p.r. 23 Park-avenue, Gordon.   |
| 1919 | P 1  | Briggs, George Henry, B.Sc., Ph.D., F.Inst.P., Assistant-Professor of Physics, University of Sydney; p.r. 13 Findlay-avenue, Roseville.   |
| 1935 |      | Brown, Ida Alison, D.Sc., Lecturer in Palæontology, University of Sydney.   |
| 1906 |      | Brown, James B., No. 1 Maitland-avenue, East Kew, E.4, Victoria.  |
| 1913 | P 20 | Browne, William Rowan, D.Sc., Assistant-Professor of Geology in the University of Sydney. (Vice-President.) (President, 1932.)  |
| 1898 |      | †Burfitt, W. Fitzmaurice, B.A., M.B., Ch.M., B.Sc. Syd., F.R.A.C.S., "Wyoming," 175 Macquarie-street, Sydney; p.r. "Radstoke," Elizabeth Bay.   |

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| 1926 |      | Burkitt, Arthur Neville St. George, M.B., B.Sc., Professor of Anatomy in the University of Sydney.  |
| 1919 | P 19 | Burrows, George Joseph, B.Sc., Lecturer and Demonstrator in Chemistry in the University of Sydney.  |
| 1934 |      | Carruthers, H. L., M.B., B.S., 4 Elcho-street, Hamilton, N.S.W.   |
| 1903 | P 3  | Carslaw, Horatio Scott, Sc.D., LL.D., F.R.S.E., Emeritus Professor of Mathematics, University of Sydney, Fellow of Emmanuel College, Cambridge; Burradoo, N.S.W.  |
| 1913 | P 4  | Challinor, Richard Westman, F.I.C., A.A.C.I., A.S.T.C., F.C.S., Lecturer in Organic Chemistry, Sydney Technical College; p.r. 54 Drumalbyn-road, Bellevue Hill. (Vice-President.) (President, 1933.)                      |
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| 1913 | P 19 | Cheel, Edwin, 40 Queen-street, Ashfield. (Hon. Treasurer.) (President, 1931.)   |
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| 1925 | P 1  | Clark, William E., 24 Cambridge-street, Epping.   |
| 1920 |      | Cooke, Frederick, c/o Meggitt's Limited, Asbestos House, York and Barrack-streets, Sydney.  |
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| 1928 |      | Coppleson, Victor Marcus, M.B., Ch.M., F.R.C.S., F.R.A.C.S., Surgeon, 225 Macquarie-street, Sydney; p.r. "Cravenna," 8 Macleay-street, Potts Point.   |
| 1933 |      | Corbett, Robert Lorimer, Managing Director of Robert Corbett & Co. Ltd., Manufacturing Chemists, Head Office, 379 Kent-street, Sydney.  |
| 1882 |      | Cornwell, Samuel, J.P., "Capanesk," Tyagarah, N.S.W.  |
| 1919 |      | Cotton, Frank Stanley, D.Sc., Chief Lecturer and Demonstrator in Physiology in the University of Sydney.  |
| 1909 | P 7  | Cotton, Leo Arthur, M.A., D.Sc., Professor of Geology in the University of Sydney. (President, 1929.)   |
| 1892 | P 1  | †Cowardery, George R., Assoc.M.Inst.C.E., Strathfield-avenue, Strathfield.  |
| 1921 | P 1  | †Cresswick, John Arthur, A.A.C.I., F.C.S., Production Superintendent and Chief Chemist, c/o The Metropolitan Meat Industry Commissioner, State Abattoir and Meat Works, Homebush Bay; p.r. 101 Villiers-street, Rockdale. |
| 1935 | P 1  | Culey, Alma Gertrude, M.Sc., 37 Neirbo-avenue, Hurstville.  |
| 1912 |      | Curtis, Louis Albert, L.S., F.I.S., V.D., Major, Surveyor, 66 Pitt-street, Sydney; p.r. 59 Albyn-road, Strathfield.   |

## Elected.

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| 1890 |      | Dare, Henry Harvey, M.E., M.Inst.C.E., M.I.E.Aust., 14 Victoria-street, Roseville.   |
| 1928 |      | Davison, Walter Charles, "Whistable," Prospect-road, Summer Hill.  |
| 1919 | P 2  | de Beuzeville, Wilfrid Alex. Watt, J.P., "Mélamere," Welham-street, Beecroft.  |
| 1894 |      | Dick, James Adam, C.M.G., B.A. <i>Syd.</i> , M.D., C.M. <i>Edin.</i> , F.R.C.S. <i>Edin.</i> , Col. A.A.M.C., Comr. Ord. St. John, Medical Practitioner, "Catfoss," 59 Belmore-road, Randwick.                 |
| 1906 |      | †Dixon, William, "Merridong," Gordon-road, Killara.  |
| 1913 | P 3  | Doherty, William M., F.I.C., F.A.C.I., "Jesmond," 36 George-street, Marrickville.  |
| 1928 |      | Donegan, Henry Arthur James, A.S.T.C., A.A.C.I., Analyst, Department of Mines, Sydney; p.r. 18 Hillview-street, Sans Souci.  |
| 1924 |      | Dupain, George Zephirin, A.A.C.I., F.C.S., Director Dupain Institute of Physical Education and Medical Gymnastics, Manning Building, 449 Pitt-street, Sydney; p.r. "Rose Bank," 158 Parramatta-road, Ashfield. |
| 1924 |      | Durham, Joseph, 9 Ada-street, Randwick.  |
| 1934 | P 7  | Dwyer, Francis P. J., M.Sc., Lecturer in Chemistry, Technical College, Sydney.   |
| 1923 | P 17 | Earl, John Campbell, D.Sc., Ph.D., Professor of Organic Chemistry in the University of Sydney.   |
| 1924 |      | Eastaugh, Frederick Alldis, A.R.S.M., F.I.C., Associate Professor in Chemistry, Assaying and Metallurgy in the University of Sydney.   |
| 1934 | P 1  | Elkin, Adolphus Peter, M.A., Ph.D., Professor of Anthropology in the University of Sydney.   |
| 1935 |      | Ellis, Leon Macintosh, B.Sc.F. <i>Toronto</i> , Union Building, Bond-street, Sydney.   |
| 1935 |      | England, Sidney Willis, 29 Queen-street, Mosman.   |
| 1916 | P 2  | Enright, Walter John, B.A., Solicitor, High-street, West Maitland; p.r. Regent-street, West Maitland.  |
| 1908 |      | Esdaille, Edward William, 42 Hunter-street, Sydney.  |
| 1935 |      | Evans, Silvanus Gladstone, A.I.A.A. <i>Lond.</i> , A.R.A.I.A., 6 Major-street, Coogee.   |
| 1921 |      | Farnsworth, Henry Gordon, Government Stores, Harrington-street, Sydney; p.r. "Rothsay," 90 Alt-street, Ashfield.   |
| 1910 |      | Farrell, John, A.S.T.C., Riverina Flats, 265 Palmer-street, Sydney.  |
| 1909 | P 7  | Fawsitt, Charles Edward, D.Sc., Ph.D., Professor of Chemistry in the University of Sydney. (President, 1919.)  |
| 1923 |      | Fiaschi, Piero, O.B.E., V.D., M.D. <i>Columbia Univ.</i> , D.D.S. <i>New York</i> , M.R.C.S. <i>Eng.</i> , L.R.C.P. <i>Lond.</i> , 178 Phillip-street, Sydney.   |
| 1927 | P 7  | Finnemore, Horace, B.Sc., F.I.C., Lecturer in Pharmacy in the University of Sydney.  |
| 1935 |      | Firth, Francis Williamson, Elliotts and Australian Drug Ltd., O'Connell-street, Sydney.  |

## Elected.

- 1935 Firth, John Clifford, B.Sc., "Avoca," Huntley's Point-road, Gladesville.
- 1920 Fisk, Ernest Thomas, F.Inst.R.E., A.M.I.E., (*Aust.*) Chairman of Directors, Amalgamated Wireless (Australasia) Ltd., Wireless House, 47 York-street, Sydney; p.r. 16 Beaconsfield-parade, Lindfield.
- 1933 Fletcher, Harold Oswald, Assistant Palæontologist, Australian Museum, College-street, Sydney.
- 1879 †Foreman, Joseph, M.R.C.S. *Eng.*, L.R.C.P. *Edin.*, "The Astor," Macquarie-street, Sydney.
- 1932 Forman, Kenn. P., M.I.Refr.E., 13 Market-street, Sydney; p.r. "Wyreema," Alison-road, Randwick.
- 1905 Foy, Mark, c/o Geo. O. Bennett, 133 Pitt-street, Sydney.
- 1935 Fraser, Lilian Ross, M.Sc., 25 Bellamy-street, Pennant Hills.
- 
- 1935 P 2 Garretty, Michael Duhan, B.Sc., Consulting Geologist, "Erskine House," 167 View-street, Bendigo, Vic.
- 1926 Gibson, Alexander James, M.E., M.Inst.C.E., M.I.E.Aust., Consulting Engineer, 906 Culwulla Chambers, Castlereagh-street, Sydney; p.r. "Wirruna," Belmore-avenue, Wollstonecraft.
- 1935 Goddard, Roy Hamilton, F.C.A. *Aust.*, Royal Exchange, Bridge-street, Sydney.
- 1921 Godfrey, Gordon Hay, M.A., B.Sc., Lecturer in Physics in the Technical College, Sydney.
- 1936 Goulston, Edna Maude, B.Sc., Demonstrator in Micro-Chemistry in the University of Sydney; p.r. 83 Birriga-road, Bellevue Hill.
- 
- 1934 Hall, Norman Frederick Blake, M.Sc., Chemist, Council for Scientific and Industrial Research (Tobacco Section), Dept. of Organic Chemistry, University of Sydney; p.r. 4 Whatmore-street, North Sydney.
- 1880 P 6 †Halligan, Gerald Harnett, L.S., F.G.S., Retired Civil Engineer and Hydrographer, "Coniston," Marian-street, Killara.
- 1912 Hallman, Edward Francis, B.Sc., Assistant Mathematical Master, Fort Street Boys' High School, Petersham; p.r. 15 Harrington-street, Marrickville.
- 1892 Halloran, Henry Ferdinand, L.S., 82 Pitt-street, Sydney.
- 1919 Hambridge, Frank, Adelaide Steamship Co. Chambers, 22 Bridge-street, Sydney; p.r. "The Chalet," Lucinda-avenue, Wahroonga.
- 1933 Hancock, Francis Charles, B.Sc. (Hons.), Dip.Ed. (*University of Bristol*), St. John's C. of E. Grammar School, Forbes-street, Darlinghurst.
- 1905 P 6 Harker, George, D.Sc., F.A.C.I., Cancer Research Department, University of Sydney; p.r. 75 Prospect-road, Summer Hill.
- 1936 Harper, Arthur Frederick Alan, 52 Primrose-avenue, Rosebery.
- 1934 Harrington, Herbert Richard, Teacher of Physics and Electrical Engineering, Technical College, Harris-street, Ultimo.

## Elected.

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|------|------|--|
| 1923 | P 3  | Harrison, Travis Henry John, D.Sc.Agr., D.I.C. ( <i>London</i> ), Lecturer in Botany and Entomology, Hawkesbury Agricultural College, Richmond.  |
| 1929 |      | Hawley, J. William, J.P., Financial Agent, 46 Martin-place, Sydney; p.r. 12 King's-road, Vacluse.  |
| 1934 |      | Hayes, William Lyall, A.S.T.C., A.A.C.I., Works Chemist, c/o Messrs. Wm. Cooper & Nephews ( <i>Aust.</i> ) Ltd., Phillip-street, Concord; p.r. 30 Cormiston-avenue, Central Concord.   |
| 1919 |      | Henriques, Frederick Lester, 208 Clarence-street, Sydney.  |
| 1935 |      | Hewitt, Frank Rupert, 7 Tindale-road, Artarmon.  |
| 1918 |      | Hindmarsh, Percival, M.A., B.Sc.Agr., Principal, Agricultural High School, Yanco.  |
| 1936 |      | Hirst, Edward Eugene, General Manager, British General Electric Co. Ltd.; p.r. "Springmead," Ingleburn.  |
| 1928 |      | Hirst, George Walter Cansdell, B.Sc., A.S.T.C. (Sc.), A.M.I.E. ( <i>Aust.</i> ), A.M.Inst.T., c/o Chief Mechanical Engineer's Office, N.S.W. Railways, Wilson-street, Redfern; p.r. "St. Cloud," Beaconsfield-road, Chatswood. |
| 1930 |      | Hodson, John S., Assoc.I.E.E., Electrical Engineer, H.M. Naval Establishments, Garden Island, Sydney.  |
| 1916 |      | Hoggan, Henry James, A.M.I.M.E. ( <i>Lond.</i> ), A.M.I.E. ( <i>Aust.</i> ), Consulting and Designing Engineer, "Lincluden," 81 Frederick-street, Rockdale.  |
| 1930 |      | Holmes, James Macdonald, Ph.D., F.R.G.S., F.R.S.G.S., Associate Professor of Geography in the University of Sydney.  |
| 1919 |      | Hoskins, Arthur Sidney, Engineer, Steel Works, Port Kembla; postal address, P.O. Box 36, Wollongong.   |
| 1919 |      | Hoskins, Cecil Harold, Engineer, c/o Australian Iron & Steel Ltd., Kembla Building, 58 Margaret-street, Sydney, Box 3375 R, G.P.O.   |
| 1935 |      | Howarth, Mark, Grange Mount, Bull-street, Mayfield, Newcastle, N.S.W.  |
| 1936 |      | Howie, Archibald, 7 Wynyard-street, Sydney.  |
| 1923 | P 3  | †Hynes, Harold John, D.Sc., B.Sc.Agr., Senior Asst. Biologist, Department of Agriculture, Box 36A, G.P.O., Sydney; p.r. "Belboore," 10 Wandella-avenue, Roseville.   |
| 1935 |      | James, Hugh, A.C.I.S., Australian Essential Oils Ltd., 115 Pitt-street, Sydney.  |
| 1929 |      | Jeffrey, Robert Ewen, A.A.C.I., Managing Director, Bardsley's Ltd.; p.r. 9 Greycliff-avenue, Vacluse.  |
| 1909 | P 15 | Johnston, Thomas Harvey, M.A., D.Sc., C.M.Z.S., Professor of Zoology in the University of Adelaide. (Cor. Mem., 1912.)   |
| 1924 |      | Jones, Leo Joseph, Government Geologist, Department of Mines, Sydney.  |
| 1935 | P 3  | Joplin, Germaine Anne, B.Sc., Ph.D., Curator of the Geological Department Museum, University of Sydney; p.r. 18 Wentworth-street, Eastwood.  |

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|      |      |  |
|------|------|--|
| 1930 |      | Judd, William Percy, 123 Wollongong-road, Arncliffe.   |
| 1911 |      | Julius, Sir George A., Kt., B.Sc., B.E., M.I.Mech.E., M.I.E.Aust.,<br>Culwulla Chambers, Castlereagh-street, Sydney.   |
| 1932 |      | Keeble, Arthur Thomas, B.Sc., Science Master, Sydney<br>Grammar School; p.r. 55 Carlotta-street, Greenwich.  |
| 1935 |      | Kelly, Caroline Tennant (Mrs.), "The Old Parsonage,"<br>Castle Hill, N.S.W.  |
| 1935 |      | Kelly, Francis Angelo Timothy, "The Old Parsonage,"<br>Castle Hill, N.S.W.   |
| 1934 |      | Kelly, Francis de Vere, Pharmacist, The Sydney Drug<br>Stores, 264 Elizabeth-street, Sydney; p.r. c/o<br>Masonic Club, 169 Castlereagh-street, Sydney.   |
| 1924 |      | Kenny, Edward Joseph, Geological Surveyor, Depart-<br>ment of Mines, Sydney; p.r. 17 Alma-street,<br>Ashfield.   |
| 1887 |      | Kent, Harry C., M.A., F.R.I.B.A., 491 New South Head-<br>road, Double Bay.   |
| 1934 |      | Kerslake, Richmond, A.S.T.C., A.A.C.I., Industrial<br>Chemist, c/o Australian Paper Mfrs. Ltd., Macauley-<br>street, Matraville; p.r. 55 Harold-street, Matraville.  |
| 1896 |      | King, Sir Kelso, K.B., Underwriter, 117 Pitt-street,<br>Sydney; p.r. "Quambi," Albert-street, Edgecliff.   |
| 1920 |      | Kirchner, William John, B.Sc., A.A.C.I., Manufacturing<br>Chemist, c/o Messrs. Burroughs, Wellcome & Co.<br>(Australia) Ltd., Victoria-street, Waterloo; p.r.<br>"Wanawong," 27 Thornleigh-road, Beecroft. |
| 1935 |      | Lawrence, Elizabeth Frances, B.A., Demonstrator in<br>Geography, University of Sydney.   |
| 1936 |      | Leach, Stephen Laurence, B.A., B.Sc., A.A.C.I., 69<br>Lithgow-street, Crows Nest.  |
| 1924 |      | Leech, Thomas David James, B.Sc., B.E. Syd., P. N.<br>Russell School of Engineering, University of Sydney;<br>p.r. 57 Clanalpine-street, Mosman.   |
| 1934 |      | Leech, William Dale, Director of Research, Australasian<br>Food Research Laboratories, Cooranbong, N.S.W.  |
| 1936 | P 1  | Lemberg, Max Rudolf, Biochemist, Royal North Shore<br>Hospital; p.r. 36 Goodchap-road, Chatswood.  |
| 1920 |      | Le Souef, Albert Sherbourne, Curator, Taronga Park,<br>Mosman; p.r. 3 Silex-road, Mosman.  |
| 1916 |      | L'Estrange, Walter William, 7 Church-street, Ashfield.   |
| 1909 |      | Leverrier, Frank, B.A., B.Sc., K.C., c/o Austral Malay<br>Tin Ltd., Challis House, Martin-place, Sydney;<br>p.r. Wentworth-road, Vaucluse.   |
| 1929 | P 14 | Lions, Francis, B.Sc., Ph.D., A.I.C., Lecturer in Organic<br>Chemistry in the University of Sydney; p.r. 31<br>Chesterfield-road, Epping.  |
| 1906 |      | Loney, Charles Augustus Luxton, M.Am.Soc.Refr.E.,<br>National Mutual Building, 350 George-street,<br>Sydney.   |
| 1927 | P 1  | Love, William Henry, B.Sc., Ph.D., Cancer Research<br>Department, University of Sydney.  |



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|------|------|--|
| 1906 | P 2  | McIntosh, Arthur Marshall, "Moy Lodge," Hill-street, Roseville.  |
| 1891 |      | †McKay, R. T., L.S., M.Inst.C.E., Commissioner, Sydney Harbour Trust, Circular Quay, Sydney.   |
| 1930 |      | Mackenzie, William Donald, F.I.C., M.I.Chem.E., F.A.C.I., Chairman and Managing Director, Messrs. Lever Brothers Ltd., Balmain; p.r. "Aston," Aston Gardens, Bellevue Hill.        |
| 1932 |      | McKie, Rev. Ernest Norman, B.A. <i>Syd.</i> , St. Columba's Manse, Guyra, N.S.W.   |
| 1927 |      | McMaster, Sir Frederick Duncan, Kt., "Dalkeith," Cassilis, N.S.W.  |
| 1916 |      | McQuiggin, Harold G., M.B., Ch.M., B.Sc., Lecturer and Demonstrator in Physiology in the University of Sydney; p.r. 11A Frenchman's-road, Randwick.                                |
| 1924 |      | Mance, Frederick Stapleton, "Binbah," Lucretia-avenue, Longueville.  |
| 1880 | P 1  | Manfred, Edmund Cooper, Architect, Belmore-square, Goulburn.   |
| 1929 | P 1  | Matheson, Alexander James, Teacher, the High School, Dubbo.  |
| 1926 |      | Mathews, Hamilton Bartlett, B.A., F.I.S., F.C.I.V., Surveyor-General of N.S.W., Department of Lands, Sydney.   |
| 1935 |      | Maze, Wilson Harold, B.Sc., Lecturer in Geography, University of Sydney.   |
| 1933 |      | Mears, Arthur Cyril Weeks, A.S.A.S.M. (Electrical and Mechanical Engineering), Engineer Commander, Royal Australian Navy, Navy Office, St. Kilda-road, Melbourne, S.C.1, Victoria. |
| 1912 |      | Meldrum, Henry John, B.A., B.Sc., Lecturer, The Teachers' College, University Grounds, Newtown; p.r. 98 Sydney-road, Manly.  |
| 1929 | P 9  | Mellor, David Paver, M.Sc., Lecturer and Demonstrator, Chemistry Department, University of Sydney; p.r. 35 Oliver-road, Roseville.   |
| 1928 |      | Micheli, Louis Ivan Allan, M.Sc., Ph.D., Research Chemist, c/o Colonial Sugar Refining Co., Pyrmont.   |
| 1926 |      | Mitchell, Ernest Marklow, A.M.I.E. <i>Aust.</i> , Civil Engineer, Metropolitan Water, Sewerage and Drainage Board, 341 Pitt-street, Sydney; p.r. 106 Harrow-road, Bexley.          |
| 1922 | P 23 | Morrison, Frank Richard, A.A.C.I., F.C.S., Assistant Chemist, Technological Museum, Sydney.  |
| 1924 |      | Morrison, Malcolm, Curator, Mining Museum, Sydney; p.r. "Tayan," Herbert-street, Rockdale.   |
| 1934 |      | Mort, Francis George Arnot, Chemist, c/o Lewis Berger & Sons Ltd., Rhodes; p.r. 16 Grafton-street, Woollahra.  |
| 1879 |      | Mullins, John Lane, M.L.C., M.A. <i>Syd.</i> , Barrister, 7 Greenknowe-avenue, Potts Point.  |
| 1915 |      | Murphy, Robert Kenneth, Dr.Ing., Chem.Eng., A.S.T.C., M.I.Chem.E., A.A.C.I., Lecturer in Charge of Chemistry and Head of Science Department, Sydney Technical College.             |

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|      |      |  |
|------|------|--|
| 1923 | P 2  | Murray, Jack Keith, B.A., B.Sc.Agr., Principal, Queensland Agricultural College, Gatton, Queensland, and Professor of Agriculture in the University of Queensland.                                 |
| 1893 | P 4  | Nangle, James, O.B.E., F.R.A.S., F.R.A.I.A., Government Astronomer, The Observatory, Sydney; Room 706, Australia House, Carrington-street, Sydney. (President, 1920.)                              |
| 1930 | P 3  | Naylor, George Francis King, M.A., M.Sc., Dip.Ed., Assistant Director, Australian Institute of Industrial Psychology, 12 O'Connell-street, Sydney; p.r. "Kingsleigh," Ingleburn, N.S.W.            |
| 1932 |      | Newman, Ivor Vickery, M.Sc., Ph.D., F.R.M.S., F.L.S., Department of Biology, Victoria University College, Wellington, N.Z.   |
| 1924 |      | Nickoll, Harvey, L.R.C.P., L.R.C.S., Terrigal, N.S.W.  |
| 1935 |      | Nicol, Phyllis Mary, M.Sc., Sub-Principal, The Women's College, Newtown.   |
| 1891 |      | †Noble, Edward George, L.S., Local Government Engineer, 8 Louisa-road, Balmain.  |
| 1920 | P 3  | †Noble, Robert Jackson, M.Sc., B.Sc.Agr., Ph.D., Biologist, Department of Agriculture, Box 36A, G.P.O., Sydney; p.r. "Warrah," 51 Boundary-street, Roseville. (Vice-President.) (President, 1934.) |
| 1935 |      | O'Connell, Daniel J. K., S.J., M.Sc., F.R.A.S., Riverview College Observatory, Sydney.   |
| 1903 |      | †Old, Richard, "Waverton," Bay-road, North Sydney.   |
| 1930 |      | O'Leary, Rev. William J., S.J., Seismologist, St. Ignatius' College, Riverview, Sydney.  |
| 1913 |      | Ollé, A. D., F.C.S., A.A.C.I., "Kareema," Charlotte-street, Ashfield.  |
| 1932 |      | O'Neill, John Patrick, F.I.I.A., F.C.I. ( <i>Eng.</i> ), Chief Timber Inspector, Department of Railways, Bridge-street, Sydney; p.r. 38 Wilberforce-avenue, Rose Bay.                              |
| 1921 | P 3  | Osborne, George Davenport, D.Sc., Lecturer and Demonstrator in Geology in the University of Sydney.  |
| 1928 |      | Parsons, Stanley William Enos, Analyst and Inspector, N.S.W. Explosive Department; p.r. Shepherd-road, Artarmon.   |
| 1935 |      | Payne-Scott, Ruby Violet, Assistant Physicist, Cancer Research Department, University of Sydney.   |
| 1920 | P 69 | Penfold, Arthur Ramon, F.A.C.I., F.C.S., Curator and Economic Chemist, Technological Museum, Harris-street, Ultimo; p.r. 25 Ramsay-road, Pennant Hills. (Vice-President.) (President, 1935.)       |
| 1933 |      | Penman, Arthur Percy, B.E. <i>Syd.</i> , Mining Engineer, 10 Water-street, Wahroonga.  |
| 1935 |      | Phillips, Orwell, "Linthgow," 4 Wentworth-street, Point Piper.   |

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|------|-----|--|
| 1919 |     | Poate, Hugh Raymond Guy, M.B., Ch.M. <i>Syd.</i> , F.R.C.S. Eng., L.B.C.P. <i>Lond.</i> , F.R.A.C.S., Surgeon, 225 Macquarie-street, Sydney; p.r. 38 Victoria-road, Bellevue Hill. |
| 1896 |     | Pope, Roland James, B.A. <i>Syd.</i> , M.D., Ch.M., F.R.C.S. <i>Edin.</i> , 185 Macquarie-street, Sydney.  |
| 1935 |     | Potts, Charles Vickers, 28 O'Connell-street, Sydney.   |
| 1921 | P 2 | Powell, Charles Wilfrid Roberts, F.I.C., A.A.C.I., Company Executive, c/o Colonial Sugar Refining Co., O'Connell-street, Sydney; p.r. "Wansfell," Kirkoswald-avenue, Mosman.       |
| 1918 |     | Powell, John, Managing Director, Foster Clark (Aust.) Ltd., 17 Thurlow-street, Redfern; p.r. "Elgarth," Ranger's-road, Cremorne.   |
| 1927 |     | Price, William Lindsay, B.E., B.Sc., Teacher of Physics, Sydney Technical College; p.r. 130 Provincial-road, Lindfield.  |
| 1918 |     | Priestley, Henry, M.D., Ch.M., B.Sc., Associate Professor of Physiology in the University of Sydney.   |
| 1893 |     | Purser, Cecil, B.A., M.B., Ch.M. <i>Syd.</i> , Physician, 185 Macquarie-street, Sydney; p.r. "Ascot," Grosvenor-road, Wahroonga.   |
| 1929 |     | Pyke, Henry George, A.S.T.C., Assistant Works Chemist, Australian Gas Light Company, Mortlake; p.r. 29 Maple-avenue, Pennant Hills.  |
| 1935 | P 2 | †Quodling, Florrie Mabel, B.Sc., Demonstrator in Geology, University of Sydney.  |
| 1922 | P 7 | Raggatt, Harold George, M.Sc., Geologist, c/o Mines Department, Sydney.  |
| 1919 | P 3 | Ranclaud, Archibald Boscawen Boyd, B.Sc., B.E., Lecturer in Physics, Teachers' College, The University, Sydney.  |
| 1936 |     | Randall, Harry, 7 Selbourne-street, Burwood.   |
| 1931 | P 1 | Rayner, Jack Maxwell, B.Sc., F.Inst.P., Physicist to the Department of Mines, Sydney; p.r. 125 William-street, Granville.  |
| 1935 |     | Reid, Andrew, "Neringah," Wahroonga.   |
| 1935 |     | Reid, Cicero Augustus, 11 Robertson-road, Centennial Park.   |
| 1928 |     | Reidy, Eugene Nicholas, A.S.T.C., Analyst, Department of Mines, Sydney.  |
| 1937 |     | Reuter, Fritz, Research Chemist, 21 Wycombe-road, Neutral Bay.   |
| 1932 |     | Richardson, Henry Elmar, Chemist, Chase-road, Turramurra.  |
| 1933 |     | Roberts, Richard George Crafter, Electrical Engineer, "Redcliffe," Liverpool-road, Ashfield.   |
| 1935 |     | Robinson, Albert Jordan, Managing Director, S. T. Leigh & Co. Ltd., Raleigh Park, Kensington.  |
| 1935 |     | Room, Thomas G., Professor of Mathematics in the University of Sydney.   |

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| 1928 |     | Ross, Allan Clunies, B.Sc., F.C.A. ( <i>Aust.</i> ), Chartered Accountant ( <i>Aust.</i> ), 54A Pitt-street, Sydney; p.r. The Grove, Woollahra. (Member from 1915 to 1924.)                              |
| 1929 |     | Royle, Norman Dawson, M.D., Ch.M., 185 Macquarie-street, Sydney.   |
| 1934 |     | Salter, Keith Eric Wellesley, B.Sc., Entomologist, Curator Macleay Museum, The University of Sydney; p.r. "Hawthorn," 48 Abbotsford-road, Homebush.  |
| 1935 |     | Savage, Clarence Golding, Director of Fruit Culture, Department of Agriculture, Sydney.  |
| 1920 |     | Scammell, Rupert Boswood, B.Sc. ( <i>Syd.</i> ), A.A.C.I., F.C.S., c/o F. H. Faulding & Co. Ltd., 98 Castlereagh-street, Redfern; p.r. 10 Buena Vista-avenue, Clifton Gardens.                           |
| 1933 |     | Selby, Esmond Jacob, Dip.Com., Sales Manager, "Marley," Werona-avenue, Gordon.   |
| 1936 |     | Sellenger, Brother Albertus, Marist Brothers' College, Randwick.   |
| 1936 |     | Sherrard, Kathleen Margaret Maria (Mrs.), M.Sc. ( <i>Melb.</i> ), 43 Robertson-road, Centennial Park.  |
| 1917 |     | Sibley, Samuel Edward, Mount-street, Coogee.   |
| 1900 |     | †Simpson, R. C., Lecturer in Electrical Engineering, Technical College, Sydney.  |
| 1933 |     | Slade, George Hermon, B.Sc., Director, W. Hermon Slade & Co. Ltd., Manufacturing Chemists, 23 Rosebery-avenue, Rosebery; p.r. "Raiatea," Oyama-avenue, Manly.  |
| 1922 | P 1 | Smith, Thomas Hodge, Australian Museum, College-street, Sydney.  |
| 1919 |     | Southee, Ethelbert Ambrook, O.B.E., M.A., B.Sc., B.Sc.Agr., Principal, Hawkesbury Agricultural College, Richmond, N.S.W.   |
| 1921 |     | Spencer-Watts, Arthur, "Araboocoo," Glebe-street, Randwick.  |
| 1917 |     | Spruson, Wilfred Joseph, M.C.I.P.A., F.I.A.P.A., c/o Spruson & Ferguson, Patent Attorneys and Consulting Engineers, 66 Pitt-street, Sydney; p.r. "Bengalala," Neutral Bay.                               |
| 1916 |     | Stephen, Alfred Ernest, F.C.S., c/o Box 1158 HH, G.P.O., Sydney.   |
| 1914 |     | Stephens, Frederick G. N., F.R.C.S., M.B., Ch.M., 135 Macquarie-street, Sydney; p.r. Captain Piper's-road and New South Head-road, Vaucluse.   |
| 1900 | P 1 | Stewart, J. Douglas, B.V.Sc., F.R.C.V.S., Professor of Veterinary Science in the University of Sydney; p.r. "Berelle," Homebush-road, Strathfield. (President, 1927.)                                    |
| 1909 |     | Stokes, Edward Sutherland, M.B., Ch.M. <i>Syd.</i> , D.P.H. <i>Irel.</i> , Medical Officer, Metropolitan Board of Water Supply and Sewerage, 341 Pitt-street, Sydney; p.r. 15 Highfield-road, Lindfield. |

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| 1916 | P 1  | Stone, Walter George, F.S.T.C., A.A.C.I., Senior Analyst, Department of Mines, Sydney; p.r. 14 Rivers-street, Bellevue Hill.  |
| 1918 |      | †Sullivan, Herbert Jay, Director in Charge of Research and Technical Department, c/o Lewis Berger & Sons (Australia) Ltd., Rhodes; Box 23, P.O., Burwood; p.r. "Stonycroft," 10 Redmyre-road, Strathfield.          |
| 1918 |      | Sundstrom, Carl Gustaf, Managing Director, Federal Match Co. Ltd., Park-road, Alexandria; p.r. 74 Alt-street, Ashfield.   |
| 1901 | P 16 | †Susmilch, C. A., F.G.S., F.S.T.C., Consulting Geologist, 11 Appian Way, Burwood. (Hon. Secretary.) (President, 1922.)  |
| 1919 |      | †Sutherland, George Fife, A.R.C.Sc. Lond., Assistant Professor of Mechanical Engineering in the University of Sydney.   |
| 1920 |      | Sutton, Harvey, O.B.E., M.D., D.P.H. Melb., B.Sc. Oxon., Professor of Preventive Medicine and Director, School of Public Health and Tropical Medicine, University of Sydney; p.r. "Lynton," 27 Kent-road, Rose Bay. |
| 1915 | P 3  | Taylor, Harold B., M.C., D.Sc., F.I.C., F.A.C.I., Second Government Analyst, Department of Public Health, 93 Macquarie-street, Sydney; p.r. 44 Kenneth-street, Longueville.   |
| 1935 |      | Tennant, Thomas Henry, Manager, Government Stores Department; p.r. 2 Borrodale-road, South Kensington.  |
| 1919 |      | Thorne, Harold Henry, M.A. Cantab., B.Sc. Syd., F.R.A.S., Lecturer in Mathematics in the University of Sydney; p.r. 55 Railway-crescent, Beecroft.  |
| 1923 |      | Tindale, Harold, General Manager, The Australian Gas Light Company, Haymarket, Sydney.  |
| 1935 |      | Tommerup, Eric Christian, M.Sc., A.A.C.I., The Ever-Ready Co., 40 Marshall-street, Surry Hills.   |
| 1923 |      | Toppin, Richmond Douglas, A.I.C., 22 Miller-street, Hurstville.   |
| 1879 |      | Trebeck, P. C., Church-street, Bowral, N.S.W.   |
| 1932 | P 7  | Trikojus, Victor Martin, B.Sc., D.Phil., Lecturer in Medical Organic Chemistry, University of Sydney; p.r. "Buxton," Tusculum-street, Potts Point.  |
| 1925 |      | Tye, Cyrus Willmott Oberon, Director of Development and Executive Officer of the Unemployment Relief Council, Treasury Building, Bridge-street, Sydney; p.r. 19 Muston-street, Mosman.                              |
| 1921 |      | Vicars, Robert, Marrickville Woollen Mills, Marrickville.   |
| 1892 |      | Vickery, George B., 9th Floor, Barrack House, Barrack-street, Sydney; p.r. "Inveresk," Coventry-road, Homebush.   |

## Elected.

|      |      |  |
|------|------|--|
| 1935 |      | Vickery, Joyce Winifred, M.Sc., Demonstrator in Botany, University of Sydney; p.r. 6 Coventry-road, Homebush.  |
| 1933 | P 2  | Voisey, Alan Heywood, B.Sc., Geologist, St. George's Hostel, West Kempsey, N.S.W.  |
| 1903 | P 8  | Vonwiller, Oscar U., B.Sc., F.Inst.P., Professor of Physics in the University of Sydney; p.r. "Appenzell," Castle Hill, N.S.W. (President, 1930.)  |
| 1936 |      | Waine, Cecil Scott, F.C.A. (Aust.), Chartered Accountant, 57 York-street, Sydney.  |
| 1910 |      | Walker, Major Harold Hutchison, Vickery's Chambers, 82 Pitt-street, Box 1723 JJ, G.P.O., Sydney.   |
| 1919 | P 1  | Walkom, Arthur Bache, D.Sc., Science House, Gloucester-street, Sydney; p.r. 45 Nelson-road, Lindfield.   |
| 1903 |      | Walsh, Fred., J.P., Consul-General for Honduras in Australia and New Zealand; For. Memb. Inst. Patent Agents, Lond.; Patent Attorney Regd. U.S.A.; Memb. Patent Law Assoc., Washington; Regd. Patent Attorn. Comm. of Aust.; Barrack House, 16 Barrack-street, Sydney; p.r. "Wals-holme," Centennial Park. |
| 1913 | P 4  | Wardlaw, Hy. Sloane Halcro, D.Sc. Syd., F.A.C.I., Lecturer and Demonstrator in Physiology in the University of Sydney.   |
| 1921 |      | †Waterhouse, Gustavus Athol, D.Sc., B.E., F.R.E.S., F.R.Z.S., 39 Stanhope-road, Killara.   |
| 1924 |      | Waterhouse, Leslie Vickery, B.E. Syd., Mining Engineer, Wingello House, Angel Place, Sydney; p.r. 4 Bertha-road, Neutral Bay.  |
| 1919 |      | Waterhouse, Lionel Lawry, B.E. Syd., Lecturer and Demonstrator in Geology in the University of Sydney.   |
| 1919 | P 3  | Waterhouse, Walter L., M.C., D.Sc.Agr., D.I.C., F.L.S., Faculty of Agriculture, University of Sydney; p.r. "Hazelmere," Chelmsford-avenue, Lindfield.  |
| 1910 |      | Watson, James Frederick, M.B., Ch.M., Canberra, F.C.T.   |
| 1911 | P 1  | Watt, Robert Dickie, M.A., B.Sc., Professor of Agriculture in the University of Sydney; p.r. 64 Wentworth-road, Vacluse. (President, 1925.)  |
| 1936 |      | Wearne, Harold Wallis, 6 Collingwood-street, Drum-moyne.   |
| 1920 | P 39 | Welch, Marcus Baldwin, B.Sc., A.I.C., Senior Research Officer, Forestry Commission of N.S.W., c/o Technological Museum, Sydney.  |
| 1920 | P 1  | Wellish, Edward Montague, M.A., Associate-Professor of Applied Mathematics in the University of Sydney; p.r. 15 Belgium-avenue, Roseville.   |
| 1921 |      | Wenholz, Harold, B.Sc.Agr., Director of Plant Breeding, Department of Agriculture, Sydney.   |
| 1935 |      | Wentworth, William Charles, 17 Wentworth-street, Point Piper.  |
| 1881 |      | †Wesley, W. H., London.  |
| 1931 |      | Wheatley, Frederick William, C.B.E., B.Sc. Oxon., D.Sc., B.A. Adel., A.S.A.S.M., 4 "Rhodesia," Macleay-street, Potts Point.  |

## Elected.

|      |      |  |
|------|------|--|
| 1922 |      | Whibley, Harry Clement, c/o Box 1860 W, G.P.O., Brisbane, Queensland.  |
| 1909 | P 3  | †White, Charles Josiah, B.Sc., Lecturer in Chemistry, Teachers' College, University Grounds, Newtown.  |
| 1928 |      | Wiesener, Frederick Abbey, M.B., Ch.M., D.O.M.S., Ophthalmic Surgeon, 143 Macquarie-street, Sydney; p.r. Jersey-road, Strathfield.                       |
| 1921 |      | Willan, Thomas Lindsay, B.Sc., Field Office, Bhamo, Upper Burma.   |
| 1920 |      | Williams, Harry, A.I.C., A.A.C.I., Chief Chemist, c/o The Lanoleen Co., Arlington Mills, Lord-street, Botany; p.r. "Southerndale," Burke-street, Oatley. |
| 1935 | P 1  | Wilson, Ralph Dudingston, M.Sc.Agr., Biological Branch, Department of Agriculture, Sydney.   |
| 1935 |      | Wolstenholme, Edmund Kay, "Petarli," New South Head-road, Double Bay.  |
| 1936 |      | Wood, Harley Weston, Assistant Astronomer, Sydney Observatory; p.r. 4 Ormond-street, Ashfield.   |
| 1891 |      | Wood, Percy Moore, L.R.C.P. Lond., M.R.C.S. Eng., "The Braes," 71 Redmyre-road, Strathfield.   |
| 1906 | P 12 | Woolnough, Walter George, D.Sc., F.G.S., Department of the Interior, Canberra, F.C.T.; p.r. "Callabonna," Park-avenue, Gordon. (President, 1926.)        |
| 1916 |      | Wright, George, Company Director, c/o Farmer & Company Limited, Sydney; p.r. "Wanawong," Castle Hill, N.S.W.   |
| 1921 |      | Yates, Guy Carrington, Seedsman, c/o Arthur Yates & Co. Ltd., 184 Sussex-street, Sydney; p.r. Boomerang-street, Turramurra.                              |

## HONORARY MEMBERS.

*Limited to Twenty.*

## Elected.

|      |  |  |
|------|--|--|
| 1914 |  | Hill, James P., D.Sc., F.R.S., Professor of Zoology, University College, Gower-street, London, W.C.1, England.   |
| 1934 |  | Howchin, Walter, F.G.S., Professor, "Stonycroft," Goodwood Park, S.A.  |
| 1931 |  | Lyle, Sir Thomas Ranken, K.B., C.B.E., M.A., D.Sc., F.R.S., "Lisbuoy," Irving-road, Toorak, Melbourne, Victoria. |
| 1915 |  | Maitland, Andrew Gibb, F.G.S., "Bon Accord," 28 Melville-terrace, South Perth, W.A.                              |
| 1912 |  | Martin, Sir Charles J., C.M.G., D.Sc., F.R.S., Roebuck House, Old Chesterton, Cambridge, England.                |
| 1930 |  | Masson, Sir David Orme, K.B.E., M.A., D.Sc., LL.D., F.R.S., 14 William-street, South Yarra, S.E.1, Victoria.     |

## Elected.

|      |  |
|------|--|
| 1935 | Murray, His Excellency Sir John Hubert Plunkett,<br>K.C.M.G., B.A., Lieutenant-Governor of Papua,<br>Government House, Port Moresby.                     |
| 1915 | Thomson, Sir Joseph J., O.M., M.A., D.Sc., F.R.S., Nobel<br>Laureate, Master of Trinity College, Cambridge,<br>England.                                  |
| 1922 | Wilson, James T., M.B., Ch.M. <i>Edin.</i> , F.R.S., Professor<br>of Anatomy in the University of Cambridge; p.r.<br>31 Grange-road, Cambridge, England. |

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 OBITUARY 1936-37.
*Ordinary Members.*

|      |                            |
|------|----------------------------|
| 1921 | Delprat, Guillaume Daniel. |
| 1920 | Fortescue, Albert John.    |
| 1897 | Gould, Sir Albert John.    |
| 1909 | Hammond, Walter L.         |
| 1919 | Kirk, Robert Newby.        |
| 1935 | McDonald, Charles Mylne.   |
| 1907 | Ryder, Charles Dudley.     |
| 1910 | Walker, Charles.           |
| 1936 | Walter, Ernest Lee.        |

*Honorary Member.*

|      |                            |
|------|----------------------------|
| 1928 | Smith, Sir Grafton Elliot. |
|------|----------------------------|

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## AWARDS OF THE CLARKE MEDAL.

Established in memory of

The Revd. WILLIAM BRANWHITE CLARKE, M.A., F.R.S., F.G.S., etc.

*Vice-President from 1866 to 1878.*

To be awarded from time to time for meritorious contributions to the Geology or Mineralogy of Australia. The prefix \* indicates the decease of the recipient.

## Awarded.

- 1878 \*Professor Sir Richard Owen, K.C.B., F.R.S.
- 1879 \*George Bentham, C.M.G., F.R.S.
- 1880 \*Professor Thos. Huxley, F.R.S.
- 1881 \*Professor F. M'Coy, F.R.S., F.G.S.
- 1882 \*Professor James Dwight Dana, LL.D.
- 1883 \*Baron Ferdinand von Mueller, K.C.M.G., M.D., Ph.D., F.R.S., F.L.S.
- 1884 \*Alfred R. C. Selwyn, LL.D., F.R.S., F.G.S.
- 1885 \*Sir Joseph Dalton Hooker, O.M., G.C.S.I., C.B., M.D., D.C.L., LL.D., F.R.S.
- 1886 \*Professor L. G. De Koninck, M.D.
- 1887 \*Sir James Hector, K.C.M.G., M.D., F.R.S.
- 1888 \*Rev. Julian E. Tenison-Woods, F.G.S., F.L.S.
- 1889 \*Robert Lewis John Ellery, F.R.S., F.R.A.S.
- 1890 \*George Bennett, M.D., F.R.C.S. *Eng.*, F.L.S., F.Z.S.
- 1891 \*Captain Frederick Wollaston Hutton, F.R.S., F.G.S.
- 1892 \*Sir William Turner Thiselton Dyer, K.C.M.G., C.I.E., M.A., LL.D., Sc.D., F.R.S., F.L.S.
- 1893 \*Professor Ralph Tate, F.L.S., F.G.S.
- 1895 \*Robert Logan Jack, LL.D., F.G.S., F.R.G.S.
- 1895 \*Robert Etheridge, Jnr.
- 1896 \*The Hon. Augustus Charles Gregory, C.M.G., F.R.G.S.
- 1900 \*Sir John Murray, K.C.B., LL.D., Sc.D., F.R.S.
- 1901 \*Edward John Eyre.
- 1902 \*F. Manson Bailey, C.M.G., F.L.S.
- 1903 \*Alfred William Howitt, D.Sc., F.G.S.
- 1907 Professor Walter Howchin, F.G.S., University of Adelaide.
- 1909 \*Dr. Walter E. Roth, B.A.
- 1912 \*W. H. Twelvvetrees, F.G.S.
- 1914 Sir A. Smith Woodward, LL.D., F.R.S., Keeper of Geology, British Museum (Natural History), London.
- 1915 \*Professor W. A. Haswell, M.A., D.Sc., F.R.S.
- 1917 \*Professor Sir Edgeworth David, K.B.E., C.M.G., D.S.O., M.A., Sc.D., D.Sc., F.R.S., F.G.S.
- 1918 Leonard Rodway, C.M.G., Honorary Government Botanist, Hobart, Tasmania.
- 1920 \*Joseph Edmund Carne, F.G.S.
- 1921 \*Joseph James Fletcher, M.A., B.Sc.
- 1922 Richard Thomas Baker, The Crescent, Cheltenham.
- 1923 \*Sir W. Baldwin Spencer, K.C.M.G., M.A., D.Sc., F.R.S.
- 1924 \*Joseph Henry Maiden, I.S.O., F.R.S., F.L.S., J.P.
- 1925 \*Charles Hedley, F.L.S.
- 1927 Andrew Gibb Maitland, F.G.S., "Bon Accord," 28 Melville Terrace, South Perth, W.A.
- 1928 Ernest C. Andrews, B.A., F.G.S., 32 Benelong Crescent, Bellevue Hill.

Awarded.

- 1929 Professor Ernest Willington Skeats, D.Sc., A.R.C.S., F.G.S.,  
University of Melbourne, Carlton, Victoria.
- 1930 L. Keith Ward, B.A., B.E., D.Sc., Government Geologist,  
Geological Survey Office, Adelaide.
- 1931 Robin John Tillyard, M.A., D.Sc., Sc.D., F.R.S., F.L.S., F.E.S.,  
Canberra, F.C.T.
- 1932 Frederick Chapman, A.L.S., F.G.S., Melbourne.
- 1933 Walter George Woolnough, D.Sc., F.G.S., Department of the  
Interior, Canberra, F.C.T.
- 1934 Edward Sydney Simpson, D.Sc., B.E., F.A.C.I., Carlingford,  
Mill Point, South Perth, W.A.
- 1935 George William Card, A.R.S.M., 16 Ramsay-street, Collaroy,  
N.S.W.
- 1936 Sir Douglas Mawson, Kt., O.B.E., F.R.S., D.Sc., B.E., University  
of Adelaide.
- 1937 J. T. Jutson, B.Sc., LL.B., 9 Ivanhoe-parade, Ivanhoe, Victoria.

#### AWARDS OF THE SOCIETY'S MEDAL AND MONEY PRIZE.

*Money Prize of £25.*

Awarded.

- 1882 John Fraser, B.A., West Maitland, for paper entitled "The  
Aborigines of New South Wales."
- 1882 Andrew Ross, M.D., Molong, for paper entitled "Influence of  
the Australian climate and pastures upon the growth of  
wool."

*The Society's Bronze Medal and £25.*

- 1884 W. E. Abbott, Wingen, for paper entitled "Water supply in the  
Interior of New South Wales."
- 1886 S. H. Cox, F.G.S., F.C.S., Sydney, for paper entitled "The Tin  
deposits of New South Wales."
- 1887 Jonathan Seaver, F.G.S., Sydney, for paper entitled "Origin and  
mode of occurrence of gold-bearing veins and of the  
associated Minerals."
- 1888 Rev. J. E. Tenison-Woods, F.G.S., F.L.S., Sydney, for paper  
entitled "The Anatomy and Life-history of Mollusca  
peculiar to Australia."
- 1889 Thomas Whitelegge, F.R.M.S., Sydney, for paper entitled "List  
of the Marine and Fresh-water Invertebrate Fauna of Port  
Jackson and Neighbourhood."
- 1889 Rev. John Mathew, M.A., Coburg, Victoria, for paper entitled  
"The Australian Aborigines."
- 1891 Rev. J. Milne Curran, F.G.S., Sydney, for paper entitled "The  
Microscopic Structure of Australian Rocks."
- 1892 Alexander G. Hamilton, Public School, Mount Kembla, for  
paper entitled "The effect which settlement in Australia  
has produced upon Indigenous Vegetation."
- 1894 J. V. De Coque, Sydney, for paper entitled the "Timbers of  
New South Wales."
- 1894 R. H. Mathews, L.S., Parramatta, for paper entitled "The  
Aboriginal Rock Carvings and Paintings in New South  
Wales."

Awarded.

- 1895 C. J. Martin, D.Sc., M.B., F.R.S., Sydney, for paper entitled "The physiological action of the venom of the Australian black snake (*Pseudechis porphyriacus*)."
- 1896 Rev. J. Milne Curran, Sydney, for paper entitled "The occurrence of Precious Stones in New South Wales, with a description of the Deposits in which they are found."

## AWARDS OF THE WALTER BURFITT PRIZE.

*Bronze Medal and Money Prize of £50.*

Established as the result of a generous gift to the Society by Dr. W. F. BURFITT, B.A., M.B., Ch.M., B.Sc., of Sydney. Awarded at intervals of three years to the worker in pure and applied science, resident in Australia or New Zealand, whose papers and other contributions published during the past three years are deemed of the highest scientific merit, account being taken only of investigations described for the first time, and carried out by the author mainly in these Dominions.

Awarded.

- 1929 Norman Dawson Royle, M.D., Ch.M., 185 Macquarie Street, Sydney.
- 1932 Charles Halliboy Kellaway, M.C., M.D., M.S., F.R.C.P., The Walter and Eliza Hall Institute of Research in Pathology and Medicine, Melbourne.
- 1935 Victor Albert Bailey, M.A., D.Phil., Associate-Professor of Physics, University of Sydney.

## AWARDS OF LIVERSIDGE RESEARCH LECTURESHIP.

This Lectureship was established in accordance with the terms of a bequest to the Society by the late Professor Archibald Liversidge. Awarded at intervals of two years, for the purpose of encouragement of research in Chemistry. (This JOURNAL, Vol. LXII, pp. x-xiii, 1928.)

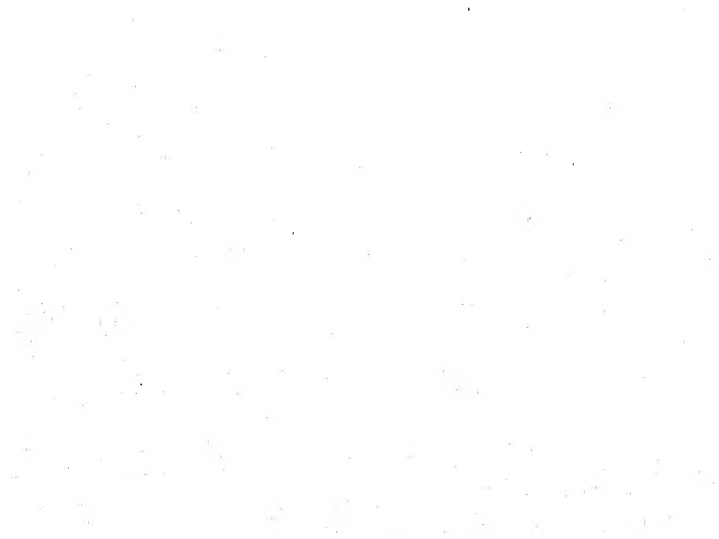
Awarded.

- 1931 Harry Hey, c/o The Electrolytic Zinc Company of Australasia, Ltd., Collins Street, Melbourne.
- 1933 W. J. Young, D.Sc., M.Sc., University of Melbourne.

### CORRIGENDA.

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In Presidential Address, p. 26, line 23, for " cineol ", read " citral ". On p. 34, footnote 15, for " THIS JOURNAL ", read *Proc. Linn. Soc. of N.S.Wales*.



# PRESIDENTIAL ADDRESS

By A. R. PENFOLD, F.A.C.I., F.C.S.,  
*Curator, Sydney Technological Museum.*

*(Delivered to the Royal Society of New South Wales, May 6, 1936.)*

## PART I. GENERAL.

Ladies and gentlemen, this is the first time in the history of the Royal Society of New South Wales that the Presidential Address has been delivered to ladies as well as gentlemen.

I intend to follow the custom established by my predecessors, and will comment on matters which have been of interest to us as members of the Royal Society of New South Wales, during the past twelve months.

The year was one of the most progressive in the long history of the Society. An epoch in its long and honourable history was the admission of women to membership of the Society on 4th September, 1935.

The admission of women to membership appears to have been of an evolutionary character, for there was nothing in the rules to prevent them from becoming members. Apparently there existed from the earliest days of the Society an indefinable barrier or atmosphere which clearly indicated that women would not be welcome. Obviously such a condition of affairs could not continue in these enlightened times. Members of the Council have for some time realised that a progressive society like the Royal Society of New South Wales would eventually have to admit women to membership. I am unable to claim any special credit for the innovation, but am pleased it should have taken place during my term of office as President. I feel sure the admission of women to membership will add greatly to the influence and prestige of the Society. At this date there are eleven women members.

Dr. R. J. Noble, in his Presidential Address for the previous year, expressed regret that only one symposium was held during his term of office.<sup>1</sup> During the past

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<sup>1</sup> JOUR. AND PROC. ROY. SOC. N.S.W., Vol. LXXIX, 1935, p. 3.  
A—May 6, 1936.

year two symposia were held, in which many speakers took part. The subjects discussed were "Sulphur" and "The Upper Atmosphere".

Symposia of this nature are much appreciated, but their success depends upon the ability of speakers to adhere strictly to the time allotted for the presentation of their particular subject. Moreover, it is imperative that the speakers present their subjects in such a manner that they will be readily understood by all members. Council has endeavoured to maintain the interest of all members by adopting this procedure—a procedure which has been of inestimable value to both authors and members; and it has been responsible for the improved attendance at the monthly meetings and the increased interest in the activities of the Society.

The necessity for the popular exposition of papers wherever practicable and within a specified time cannot be over-emphasised.

The lecturettes on recent developments in various branches of pure and applied science have been appreciated, and should be extended. These lecturettes provide an additional medium for maintaining the interest of members, especially our new members, who represent many diverse interests.

The usual series of popular lectures held during the months of July, August, September and October were delivered again this year to very appreciative audiences. They were well attended by the members of the Society and the general public.

The financial position of the Society, as revealed by the Honorary Treasurer's report, has greatly improved, and may be considered very satisfactory. The Balance Sheet and Revenue and Expenditure Account presented to you this evening represents a fair presentation of the Society's true financial position. As pointed out by the Honorary Treasurer, a number of very important adjustments were found to be necessary. The Council has exercised careful oversight of all expenditure, but the improvement can be attributed to the increase in membership, reductions of outstanding subscriptions, and to the partial restoration of the Government subsidy. I take this opportunity of expressing our thanks to the Premier, the Honourable B. S. B. Stevens, and the Minister for Education, the Honourable D. H. Drummond, M.L.A., to whose interest is due the increase of £75 in the annual

grant. As you are aware, the grant was at one time £400, but was reduced in 1931 to £200.

It is pleasing to report a considerable increase in the membership of the Society from 272 in May, 1935, to 300 at the present time. The Council soon after its election gave serious consideration to the decrease in membership and proceeded to issue a private communication to a number of citizens of good standing interested in the objects of the Royal Society of New South Wales.

We were surprised to find the extent of the popular misconception as to the nature and activities of this Society. Apparently it was assumed that membership was confined to those engaged solely in scientific pursuits, whereas membership is open to all citizens of standing interested in the objects of the Society. The issue of the letter resulted in the admission of many new members to the Society. The Society suffered the loss of six members by death and ten by resignation, while eight were struck off the roll. Consequently, it was necessary for the admission of a considerable number of new members, 48 in all, to offset the total loss of 24 referred to.

In August, 1935, the Faculties of Agriculture and Veterinary Science at the University of Sydney celebrated the silver jubilee of their foundation. It afforded the Society very much pleasure to add their congratulations to those of the Government of New South Wales, the Senate of the University of Sydney, and many other important institutions, to Professor R. D. Watt, Dean of the Faculty of Agriculture, and Professor J. D. Stewart, Dean of the Faculty of Veterinary Science, on their achievement. Both Professors are esteemed members of the Council, and it is very gratifying that recognition should be accorded both these gentlemen for the services they have rendered to the primary industries, not only of the State, but of the Commonwealth of Australia.

The Council was pleased to learn of the compliment paid to the oldest member, Judge J. P. Backhouse, by the presentation of his portrait to the University of Sydney. It is of interest to record that Judge Backhouse has been a member of the Senate of the University since 1892.

The suggestion of our immediate past President, Dr. R. J. Noble, that a short explanatory notice concerning the respective papers should be included on the monthly notice paper has been adopted with success.



Various alterations in the rules were ratified at the last annual meeting held in Science House on 1st May, 1935. These alterations not only removed certain anomalies and inaccuracies, but clearly defined the duties of the hon. treasurer, increased the number of monthly meetings in the year by providing for an additional one to be held in April, and made possible the election as life members without payment of further subscriptions persons who had been members of the Society for over forty years.

Early in the year Mr. Harry Williams was appointed by the Council to act as Joint Honorary Librarian with Professor J. C. Earl, whose duties as Dean of the Faculty of Science limited the amount of time he could spare for directing the work of the Society's library. Periodicals in the library are now indexed and readily accessible to members, but there remains a great deal of work to be accomplished, particularly in connection with the completion of series of periodicals which are at present imperfect. The improvement in the library will not be made known to outside organisations and other libraries until the new supplement to the "Catalogue of Scientific Periodicals in Australian Libraries" is published. Meanwhile, a list of periodicals regularly received by the library has been printed and distributed to members.

I was pleased to represent the Society at a function of considerable historical interest which took place at Wahroonga on 14th December, 1935. A monument was unveiled to commemorate the receipt of the first direct wireless message from the United Kingdom at Wahroonga on 22nd September, 1918. One of our members, Mr. E. T. Fisk, played a foremost part in this achievement. I think this significant event is worthy of record, for the chief speaker at the unveiling ceremony was the illustrious Marchese Marconi. It is very gratifying to observe the tribute paid to Mr. Fisk as a virtual leader of the science of wireless in Australia by the *Sydney Morning Herald* in a leading article on the 21st December, 1935.

A conversazione which was well attended was held on 12th August, 1935, in Science House. The guest of honour and speaker on the occasion was Dr. H. Brose. It was proposed to hold two or more conversaciones each year in order to increase the social activities of the Society, but up to the present Council has not been successful in learning if it is the desire of the members to continue these functions.

The Walter Burfitt prize and medal were awarded in December, 1935, to Associate-Professor Victor Albert Bailey, M.A., D.Phil., for his research work in physics, radio, and the application of mathematical and statistical methods in biology.

On 13th March, 1936, the Society collaborated with other scientific societies of the State in celebrating the centenary of Charles Darwin's visit to Australia. A meeting was held in the Union Hall of the University of Sydney, at which addresses were delivered by various speakers.

The Clarke Memorial lecture entitled "The Aeroplane in the Service of Geology" was delivered by W. G. Woolnough, D.Sc., at Science House, on 20th March, 1936. This was the first time since 1918 that a Clarke Memorial Lecture had been delivered.

The Clarke Memorial Medal for the year was awarded to George W. Card, A.R.S.M., in recognition of his important contributions to the knowledge of mineralogy and petrology of this State.

The Annual Dinner was held at David Jones' Auditorium on 23rd April, 1936, and was well attended, 110 members and guests being present. It is a matter for regret that the Right Honourable J. A. Lyons, M.P., P.C., Prime Minister, was unable to be present owing to a Cabinet meeting. The principal guests included the Hon. D. H. Drummond, M.L.A., Minister for Education, Professor F. E. Lloyd, Emeritus-Professor of Botany at McGill University, Montreal, and Mrs. Lloyd, Mr. R. J. Boyd (President, Institution of Engineers, Australia), Mr. C. A. Sussmilch (President, Linnean Society of New South Wales), the Consul-General for Czechoslovakia and Mme. Kveton, Mr. F. H. Corke, representing the Chamber of Commerce.

I am deeply indebted to all members of the Council for their loyal support and helpful co-operation. I also record my appreciation of the valuable service rendered by the Executive and of the efficient manner in which Major Edgar H. Booth performed the duties of Hon. (business) Secretary. I wish to acknowledge the advice and guidance tendered to me by our Auditor, Mr. Conrad F. Horley, and to express appreciation of his personal interest in the Society's welfare.

It is with regret that I have to record the deaths of the following members :

WILLIAM JOHN ADAMS, M.I.Mech.E., died on the 12th June, 1935, in his 83rd year. He was born in England, and came to Australia in 1884, when he founded William Adams & Co. Ltd., of which he was chairman of directors up to the time of his death. In addition to his association with William Adams & Co. Ltd., he was chairman of directors of William Adams Steel Reinforcement Co. Ltd., and a member of the directorate of several other companies. Mr. Adams had been a member of this Society since 1904.

HENRY JOHN WOLBERTON BRENNAND, B.A., M.D., Ch.M. (Syd.), V.D., who died on the 11th April, 1936. Dr. Brennand was a retired surgeon-captain of the Royal Australian Navy and an assistant commissioner of the St. John Ambulance Association. He had been a member of the Society since 1891.

WILLIAM HENRY CRAGO, M.R.C.S. (Eng.), L.R.C.P. (Lond.), died on the 6th February, 1936, at the age of 85 years. Dr. Crago was born in Cornwall, and came to Australia when he was fourteen. He later returned to London, where he graduated in medicine and surgery in 1883. He returned to Australia and practised at Woolloomooloo, and later in College Street. With Sir Alexander MacCormick, Dr. E. T. Thring, and Dr. E. J. Jenkins, he founded the Terraces Hospital, which is now the Scottish Hospital. He was particularly active in the work of the Church of England Homes, and of the Deaf, Dumb, and Blind Institution. He was an honorary surgeon at the Women's Hospital and the Sydney Hospital.

In 1929, at the third session of the Australasian Medical Congress, Dr. Crago was awarded the gold medal of the British Medical Association. This medal has been awarded to only two other members in Australia. Dr. Crago became a member of the Association in 1884, and had served it as a member of Council since 1889, as honorary treasurer from 1889 to 1931, with the exception of one year, 1894, when he was president of the Branch. Dr. Crago played an important part in the arrangements for the building of the B.M.A. premises in Macquarie Street, as he had in the planning of the Association's previous headquarters in Elizabeth Street. He was manager of the "Australian Medical Gazette" from 1895 to 1914, and from 1913 to 1924 he was chairman of directors of the Australasian Medical Publishing Co. Ltd.

Dr. Crago became a member of this Society in 1886, and in 1935 was elected an honorary life member.

FRANCIS GOULDER, A.S.T.C., A.A.C.I., died on the 25th October, 1935, in his 44th year. He was the factory manager of the Ever-Ready Co. (Australia) Ltd., having been actively engaged with the company for twenty-nine years, except for a period from 1915 to 1918, when he was on active service with the 1st Field Company of the Australian Engineers. He was a councillor of the Sydney Technical College Chemical Society, and had been a member of this Society since 1932.

GEORGE INGLIS HUDSON, J.P., F.C.S., died on the 15th April, 1936. Mr. Hudson had been managing director of the Eumenthol Chemical Company, and had formerly resided in Ipswich, Queensland. He had been a member of the Society since 1913.

FREDERICK POATE, F.R.A.S., L.S., died on the 3rd December, 1935, at the age of eighty. He was born at Clanfield, England, and was educated at Gosport. When eighteen years of age he went to Hong Kong and joined the Surveyor-General's staff, eventually becoming surveyor in charge of the ordnance survey of Hong Kong and British Kowloong. After three years he resigned through ill health. He came to New South Wales and joined the Lands Department in 1877. He passed the licensed surveyors' examination and worked in the Tamworth district till 1880, when he was appointed trigonometrical surveyor. From 1882 to 1885 he organised and supervised the detail survey of Sydney. From 1889 to 1899 he was a district surveyor, and then became chairman of the Land Board. In 1910 he was appointed assistant chief surveyor, and, in 1911, Surveyor-General and Chief Surveyor. He retired in 1917.

Mr. Poate was made a Fellow of the Royal Astronomical Society of England in 1912, and was a trustee of the Australian Museum for some years. He was elected a member of this Society in 1881, and, only a few months before his death, was made a life member of the Society.

## PART II. SOME MATTERS OF NATIONAL IMPORTANCE.

In the very early days of the Royal Society of New South Wales it was the President's prerogative, at the termination of his year of office, to give a resumé of the progress in science during the past year. This has been

done of comparatively recent years, although as far back as 1877 the difficulty of presenting a first-hand account of the recent advances in all branches of science was pointed out. I have no desire to undertake this herculean task, firstly because it is practically impossible for any one individual to give an adequate and authoritative account of more than one branch of science, and secondly because the specialised and extensive literature now available readily meets all demands.

I am anxious to give an address which will be of interest to all members of the Society, and not one of a highly specialised character which must, of necessity, appeal to a very few. Before proceeding, however, to the particular subject selected, I wish to comment upon some aspects of a few of our primary products on account of their great national importance. I am of the opinion that the Society should evince a greater interest in matters of national character. Our objects clearly indicate that the Society should interest itself in such subjects as tend to develop the resources of Australia.

#### MOTOR FUEL.

As a chemist, I consider the most important technical development during the year from a national standpoint to be the installation of a new distillery at the Broken Hill Proprietary Steel Works at Newcastle, resulting in the production of approximately 40,000 gallons of benzol per week. This quantity represents but a fraction of the country's requirements in motor fuel, but is a step in the right direction. Speaking of motor fuel leads me to comment upon the production of oil from coal. The Minister in Charge of Development (Senator McLachlan) is to be congratulated upon his recently expressed opinion "that the hydrogenation process of obtaining oil from coal was the best for Australia and it would be folly for the Commonwealth Government to embark upon a huge expenditure until the process had been thoroughly tried in Great Britain and elsewhere". (*Sydney Morning Herald*, 4th January, 1936.)

At the risk of reiteration I feel in duty bound to stress the importance of Senator McLachlan's utterance, as he has disposed once and for all of the numerous representations made to the Commonwealth Government to undertake expensive experimental work on the hydrogenation of Australian coal. Convincing evidence of the soundness of

Senator McLachlan's opinion is furnished by the account of the coal hydrogenation plant at Billingham owned by Imperial Chemical Industries Ltd. This plant has a capacity of 150,000 tons of petrol per annum, which will require 600,000 tons of coal for its production. The account published in *Engineering*, 25th October, 1935, pp. 400-402, gives a very good indication of the magnitude and importance of the enterprise undertaken at Billingham. Sir Harry McGowan revealed at the opening ceremony that when time had proved the soundness of the project it was likely that similar large plants would be erected in other parts of the country.

He also pointed out that the financial risk could not be disregarded, especially as a considerable difficulty concerned the suitability of each type of coal, the determination of which had necessitated and would involve elsewhere much expensive research work. This costly plant is essentially an experimental work being conducted on behalf of the nation, and Australia would be well advised to await the results of this enterprise before committing herself to costly experimental work, which, after all, was already being undertaken without cost to herself.

#### WOOL AND SYNTHETIC FIBRES.

Another subject of considerable importance to Australia which has given rise to much controversy is the menace to our wool industry through the increasing use of synthetic fibres. Opinion is divided on the question, but during the past year several expert observers have expressed alarm at the rapidly extending use of substitutes for wool. These substitutes, sold under various names such as "Wollstra", consist of wool, about 50 per cent., in admixture with vistra from beechwood and similar hardwood pulp.

When the issue was first raised in March, 1935, I found it incumbent upon me to support the view of Mr. A. E. Heath, Official Representative for the New South Wales Government in London, who uttered the first warning, and finally the opinion of Lord Barnby, who, on 2nd December, 1935, expressed the belief that the development of the synthetic fibre industry in the great industrial centres of Europe constituted a menace to the prosperity of Australia.

Germany's inability to pay cash for wool has created a serious position and given a fillip to the utilisation of

synthetic fibres. This has given rise to the question of bartering, but up to the present without much success, for, after all, barter can be only a temporary expedient. There is grave danger that a nation like Germany, if compelled to do without wool for a prolonged period, will become so accustomed to doing without it as to have no desire to again purchase the product, certainly not so extensively as before.

The expressed view of the *Sydney Morning Herald* that it is better to maintain the good will of tried customers by facilitating their trade with us, has much to commend it. In my letter to the *Sydney Morning Herald* of 18th March, 1935, I stressed the fact that Australia is so dependent upon the export of wool that no effort should be spared to effect some satisfactory trading arrangement whereby Germany will be enabled to resume her normal purchase of wool.

The probability of the economic production of synthetic wool is more remote, but the wool growers of Australia would be well advised to keep ever before them the wizardry of the modern chemist. There is always the possibility that some skilled textile chemist will produce either a new fibre or improve an existing fibre which will possess similar insulating and resilient properties to wool without some of its disadvantages. Moreover, prices need to be maintained at a reasonable level, otherwise any pronounced rise in price will provide the desired stimulus for the chemist to exercise his wizardry.

Towards the end of 1935 it appeared as if the wool growers were satisfied to continue their complacent attitude, and to ignore the warnings of expert observers in the mistaken belief that wool was a necessary commodity, and that other nations were compelled to purchase wool irrespective of all other considerations. Consequently, I was particularly pleased to note the decision of the Australian Woolgrowers' Council and the Graziers' Federal Council (*Sydney Morning Herald*, 29th January, 1936, p. 14) to raise a special fund for wool publicity and research. The findings submitted to the joint conference held in Melbourne on 28th January, 1936, showed that the consumption of wool has declined because of the increased production and sale of artificial fibres. It was also pointed out that the decreased spending power of the people rendered necessary the use of cheap materials and the displacement of wool, silk and cotton in the textile trade

through the general attractiveness and lightness of rayon cotton.

World-wide publicity is going to be a very effective means of propaganda, but even this will not be as effective as anticipated unless Australia can supply the goods. Apart from publicity, however, research is desired in order to improve the quality of woollen goods, especially those manufactured in Australia. The Annual Report of the Department of Scientific and Industrial Research of Great Britain for 1934-1935 directed attention to the considerable progress which has been made in perfecting for use on the commercial scale the process developed in the laboratory of the Wool Industries Research Association for the production of shrinkage-resisting wool. Only by such means and the maintenance of suitable prices can the wool industry be saved to Australia.

I have discussed this particular question of wool and wool substitutes at some length because wool is easily the most valuable of our exports. The importance of the matter is again stressed by a recent statement attributed to Mr. A. E. Heath upon his return from the Leipzig Fair on 12th March, 1936.<sup>2</sup> Mr. Heath said: "Despite the statistically impregnable position of Australian wool, it was desirable to watch closely the position of Germany because of the increasing vested interests in 'Wollstra' and Germany's absence of export credits which is forcing the nation to intensify the production of substitutes for many classes of goods."

Before proceeding to the more specialised aspect of my address, I feel it is expected of me, as a worker in the domain of chemistry, to say something about any great achievement in that branch of knowledge which has taken place of recent years.

#### PRINCIPAL ACHIEVEMENT IN ORGANIC CHEMISTRY.

I consider the greatest achievement in chemistry during 1935, and, in fact, one of the greatest romances of modern organic chemistry, to be the work accomplished in the complete structural elucidation and artificial preparation of the sex hormones. Professor L. Ruzicka, to whom we are indebted for a series of classic investigations with various collaborators, has contributed an illuminating account of the male sex hormones to the *Journal of Chemical*

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<sup>2</sup> *Sydney Morning Herald*, 13th March, 1936.



*Education*, January, 1936, pp. 3-6. (See also *Nature*, 15th February, 1936, 137, p. 260.)

The relationship of the sex hormones to cholesterol is interesting, and Professor Ruzicka's hypothesis of the origin of both male and female hormones in the animal organism published in the journals referred to is indeed intriguing. The pure sex hormones which have been prepared must play a very important rôle in the medicine of the future.

### PART III. THE PRESENT POSITION OF THE FOREST PRODUCTS OF AUSTRALIA.

A perusal of the Society's Journal from 1862 to date reveals an extraordinarily wide range of diverse subjects which have constituted presidential addresses of so many distinguished predecessors of the office. Many of these are of very great value, and represent classic discourses on subjects which have exerted considerable influence on the development of this great continent.

However, no previous occupant of the chair appears to have dealt with the subject "The Present Position of the Forest Products of Australia", which is the title of my address this evening.

#### TIMBER.

From the earliest days of the foundation of the colony interest was evinced in the economics of the forests: the first article of export in 1788 was a sample of eucalyptus oil distilled from the well-known Sydney Peppermint, *Eucalyptus piperita*, growing on the shores of Port Jackson.

Naturally, the major and most important forest product is timber. The first settlers had occasion to utilise the native timber for shelter, and ever since those early days we have heard of the tremendous waste of timber which has resulted from settlement on the land. The importance of timber needs no emphasis by me; the fact that every State of the Commonwealth has a Department of Forestry is sufficient evidence of its national value.

One of the most important and comprehensive documents setting forth the position of timber supply, consumption, and marketing, is that prepared by Mr. H. R. Gray, of the Commonwealth Forestry Bureau, and submitted to the Fourth British Empire Conference held in South Africa in 1935. This publication shows that the total annual production of native timber in the Commonwealth of Australia

amounted to between 226,000,000 and 266,000,000 cubic feet, of which hardwood constituted about 80 per cent. and softwoods 20 per cent. The value of this quantity of timber was approximately £2,850,000.

It would be unwise for me to attempt to give you a list of the timbers which are exploited, the cost of production, the revenue from royalties and other statistical information, because it can all be readily obtained from the admirable series of annual reports issued by the Directors of Forestry in all the States of the Commonwealth and the Official Year Book of the Commonwealth. I am mainly concerned with certain broad aspects of the utilisation of timber as it affects the nation.

The Director of the Queensland Forest Service has directed attention to the ratio of production of timber from Crown lands and private property and shown the latter to be from three to six times that from Crown land. The position, however, is becoming serious, as the report for the year ended 30th June, 1935, directs attention to the record cut of 143,000,000 super. feet of logs from Crown lands, mainly Hoop and Bunya Pine. This is interpreted not as an indication of increased activity of the building trades, but as a proof that practically little privately owned timber remains in the State. It is pleasant to note that a vigorous planting programme of Hoop Pine and Bunya is proceeding.

The Forestry Commission of New South Wales is giving considerable attention to the regeneration of our hardwood forests and has commendably taken steps to reduce to a minimum the planting of exotic conifers.

I hope I shall not again witness the destruction of a hardwood forest for the express purpose of planting conifers—the success of which is problematical.

The Minister for Forests, New South Wales, is to be congratulated upon his praiseworthy efforts to conserve the forest resources of the State. Definite evidence of the State Government's progressive policy was afforded by the official dedication of the first national State forest at Coopernook by the Honourable B. S. B. Stevens, Premier of New South Wales, on 1st February, 1936. The forest comprises 16,040 acres, called the Manning River National Forest, and is the first to be declared since the passing of the Forestry (Amendment) Act of 1935.

The question of reafforestation has been laboured a great deal of recent years, and need not be further stressed

by me. The fact remains that there is still a great deal to learn about the fundamental properties of timber, and a considerable amount of work on the chemical and physical properties of Australian woods has been accomplished by the Sydney Technological Museum, and by the Council for Scientific and Industrial Research since its establishment in 1926. The researches into the mechanical and physical properties of Australian woods and the determination of shrinkage and other fundamental investigations, have been prosecuted with considerable vigour by the Technological Museum, and a very active programme of work is also outlined by the chief of the Division of Forest Products of the Council for Scientific and Industrial Research. The field of investigation is a very wide one, and it is a matter for regret that the Commonwealth Council for Scientific and Industrial Research has not yet seen its way to assist the Technological Museum in its work on Australian woods, a field of investigation it has pioneered with conspicuous success for over forty years. Some more practical form of co-operation is required other than an arrangement whereby overlapping of investigations is avoided.

The Technical Education Commission, in its report to the Premier of New South Wales under date 31st May, 1934, stressed the desirability of some form of co-operation between the C.S.I.R. and the Timber Research Department of the Sydney Technological Museum.

Mr. S. L. Kessell, Conservator of Forests, Western Australia, in his report to the Government of New South Wales on forestry in New South Wales, under date June, 1934, directed attention to the numerous utilisation problems awaiting solution, and stressed the fact that many developments were necessary before timber producers could claim that the forests are being worked in the most economical manner and that the timbers of New South Wales are marketed in a satisfactory condition.

We have not heard so much of recent years about the great timber famines with which we were supposed to be threatened, and this question of future supply is one which must necessarily engage the attention of forestry authorities.

Looking at the question from the point of view of a layman, it would appear that the increasing use of substitutes for timber, especially for building, such as iron, steel, concrete and plastics, will offset to some extent

the increased consumption of timber due to increase of population. Nevertheless, apart from the question of reafforestation is the reduction of losses by fire and more efficient methods of grading, seasoning and standardisation, which must necessarily result in the conservation of those great natural resources.

There has, apparently, been very great wastage in the past in the handling of our timbers from the forest to the consumer. A perusal of the various forestry reports shows that the Directors of Forests are desirous of stimulating business in timbers after the decline which has resulted from the depression, and also from the inroads made in the use of timbers by substitutes. It is felt, however, that an increasing study of wood structure, wood chemistry and timber physics must ultimately lead to an increased utilisation of Australian woods. In this direction the New South Wales Government is to be commended for its action in stimulating the use of Australian woods. There is a clause in the State Government contracts which makes it clear that Government departments must, wherever practicable, order Australian timbers, and that very special reasons must be given if an imported timber is requested. In this connection, too, there is considerable scope for the better training of artisans on the properties of Australian timbers and the technique required for their efficient working and utilisation. Instruction in the various courses of training are given on oregon, redwood and other imported timbers which are easily worked, and, consequently, these trainees, in the absence of special instruction, do not appear to be able to adapt themselves readily to any altered technique required in the handling of Australian woods.

A point in the utilisation of timbers which has, apparently, been overlooked is the possibility of using New South Wales hardwoods in smaller sizes because of their higher strength properties, in place of the imported softwoods. As a matter of fact this question is already being investigated, and it is expected that hardwoods of reduced sizes,  $4" \times 1\frac{1}{2}"$ , will be used to replace  $4" \times 2"$  oregon in various Government buildings, thus providing greater strength and stiffness, with comparatively little increase in weight.

One of the utilisation problems which is urgently in need of investigation is the determination of the properties of second growth hardwoods, frequently termed immature

eucalypts. The virgin forests are, of course, being depleted, and it is quite obvious that the time is not far distant when we will not be able to grow trees to the age of the virgin forests, and will be compelled to utilise these second growth hardwoods.

#### STABILISATION OF TREE NAMES.

One of the greatest handicaps to the utilisation and marketing of Australian timbers is the variable names given to the individual species. On account of the importance of the problem and the retarding influence it has had on the development of the forest products of Australia, I propose to discuss the question at some length.

The confused condition of the botanical nomenclature has definitely hindered the economic exploitation of our timbers. I can go further and state that the sandalwood oil industry of Western Australia has been hampered and markets lost for the oil by the constant shuffling and re-shuffling of the name of the principal tree from which the oil is extracted.

Mr. S. L. Kessell, in the report referred to,<sup>3</sup> stated:

“A problem of considerable practical importance in the forests of New South Wales is the naming of tree species, which in the case of the Eucalypts has proceeded to such an extent that even those who have made a close study of the subject are very doubtful concerning the correct botanical name of many common trees. This may be due principally to the nature of the genus, but the confusion has been multiplied by botanists who are content to create new species from small herbarium specimens without interesting themselves sufficiently in the appearance and character of the trees in the forest.

“Great service will be rendered to forestry in New South Wales by a competent botanist who undertakes the review of the nomenclature of this genus with the object of establishing as species, definite types, which can be distinguished in the field and reducing the great multiplicity of existing species, between which very fine lines have to be drawn, to the rank of varieties.”

The officers of the Sydney Technological Museum had some years before this date expressed themselves very frankly on the position which had arisen through the

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<sup>3</sup> S. L. Kessell, Report to Government of N.S.W. on Forestry in N.S.W., June, 1934.

action of some systematic botanists in naming species on very slender morphological evidence, and, in many instances, without examining the trees or plants in their native habitat. The matter was first brought under notice by Mr. M. B. Welch, B.Sc., A.A.C.I., at the meeting of the Australasian and New Zealand Association for the Advancement of Science, held in Sydney in August, 1932. A certain amount of progress was made by the sub-committee appointed to investigate the complaint, but owing to the opposition of some of the botanists concerned the matter did not appear to be pressed. I might mention at the outset of this discussion that I am not unmindful of the obligation on the part of botanists to respect the various international botanical rules whereby priority of publication must take precedence over all other considerations. This is quite satisfactory so far as ordinary plants are concerned, but it becomes a very serious matter when systematic botanists proceed in the strict application of the priority rule without exercising any commonsense in its application to economic plants. Consequently, there is a definite and widespread revolt against what can be termed the irresponsibility of systematic botanists, and this took the form of a series of resolutions which were submitted to the Sixth International Botanical Congress, held at Amsterdam from 1st to 7th September, 1935. Two proposals embodying the principle of the conservation of specific names were offered, one by Mr. J. Adams, Botanist, Central Experimental Farm, Ottawa, Canada, the other by Professor R. S. Troup, on behalf of thirty-eight forestry departments and other institutions and individuals interested in the conservation of long-used names of trees and other plants of economic interest.

I understand that before the Congress met in open session the Permanent Bureau of Nomenclature had considered the various proposals on nomenclature sent into the Congress, and rejected these two, the first by seven against and four in favour, and the second by six against and two in favour. (Three members refrained from voting on the last-mentioned motion.)

Dr. Sprague and other members of the Permanent Bureau recommended that the principle involved should be discussed, in as much as it was one that intimately concerned workers in applied botany, but after discussion the Congress rejected the principle by 208 votes to 61.

A further motion was proposed by Mr. Ramsbottom, Keeper of Botany at the British Museum of Natural History, with an addition by Dr. Randall, that an international committee should be appointed to draw up a list of names of economic plants sanctioned by an international committee, a separate list to be printed in the appendix if necessary, i.e. if asked for by the interested section of botanists; fixity of specific epithet, not specific name, is what is really wanted. The fixed specific names would not be in the interests of taxonomy. This list may remain in use for a period of ten years. This proposal was accepted, and a sub-committee to deal with the nomenclature of economic plants was appointed to deal with these lists.

This is certainly a step in the right direction, and as the list to be composed is to be published and remain valid for at least ten years, and many of us hope indefinitely, it is anticipated that systematic botanists will realise the strong feeling prevailing against them.

Members of this Society who are not vitally interested in the question of the stabilisation of tree names may not appreciate fully the serious nature of individual botanists being permitted to change the names of trees of commercial importance, for example the eucalypts, from names by which they have been known to foresters, sawmillers and others for many years. Take, for example, the well-known River Red Gum, *Eucalyptus rostrata*; it is proposed to change this euphonious name to *Eucalyptus camaldulensis*, and the other Red Gum, *Eucalyptus tereticornis*, to be changed to *umbellata*. Both the original names have been in use for over a century.

Professor A. J. Ewart, in a discussion in the *Victorian Naturalist* during the months of August, September, October and December, 1935, defined the position so clearly that I am constrained to quote him in detail:

"A point that systematists are often apt to forget is that a species has no real existence at all, but is merely a convenient mental abstraction to indicate a group of plants which are closely related to one another, but not all necessarily precisely alike. The important thing in nomenclature is not whether we use the names of species or of varieties to indicate such groups, but that we should all mean the same thing when we use the same name; in other words, stability of nomenclature is more important than the names themselves . . .

"It cannot be in the interests of science to cause unnecessary difficulties to other workers. Once a name has been applied to a particular collection of plants, only the very gravest reasons should warrant the change of that name; for instance, a difference of opinion as to whether a particular collection of plants is a species or a variety is a matter of little moment, and hardly worth disturbing existing names, if they have been long accepted and in general use. It is only when species names indicate relatively large or comparatively well-defined groups of plants that they are of much importance from a scientific point of view . . .

"To put the matter in a few words, the most important things in nomenclature are: (i) that we should all use the same names for the same things, (ii) that when names are once established and generally used, they should not be altered except for the weightiest reasons, (iii) that if the groups called 'species' are much subdivided it becomes less and less worth while giving them names, and (iv) that those who work with plants should have some voice in determining stability of nomenclature as well as those whose interest in the plant to some extent ceases once it has been given a name.

"The power of radically altering the nomenclature of an important group of plants is a very weighty responsibility to leave in the hands of a single individual. It is possible that, in the course of time, we may find small sub-committees on nomenclature set up in each country, and working through a central international committee. It would be the business of these sub-committees to approve or disapprove of all proposed changes in nomenclature . . .

"As things are, it seems likely that we will have pronounced differences of opinion for many years to come as to the naming of Eucalypts, and until some general agreement is gradually arrived at there is bound to be much confusion, to the disadvantage of all those who deal with Eucalypts, either from a scientific or an economic standpoint."

All those who have the stabilisation of tree names at heart are desirous of assisting the systematic botanists in their investigations, but, on the other hand, there should be more practical co-operation between them and the applied botanists. No doubt mistakes which need rectification have been made in past years by systematic botanists, but the modification of these errors should not be left in



the hands of one individual, but be reviewed by a committee before publication. These committees are already in operation in horticultural organisations in order to prevent multiplication of garden varieties, and they have functioned with great success, to the benefit of all concerned.

So far as the eucalypts are concerned, the proposed name changes which have recently been suggested by systematic botanists led to such a storm of protest in Australia that proposals are now afoot to draw up a list of standard botanical names, ignoring botanical rules as set down by recent botanical congresses, and to use these names for all practical purposes. It simply means that if these standard names are accepted by the Forestry Departments of the Commonwealth, State Government Departments and the Commonwealth Council for Scientific and Industrial Research, it will be sufficient for all practical purposes; it should result in uniformity of nomenclature for trees and plants of economic importance, and it will not matter materially if some of the systematic botanists who will be in the minority fall into line or not.

An indication of the world-wide nature of the movement for the stabilisation of tree names is afforded by an abstract of a paper read at a meeting of the Section of Morphology and Anatomy, Sixth International Botanical Congress, Amsterdam, 3rd September, 1935, by Professor S. J. Record, entitled "Some Problems for the Wood Anatomist", published in *Tropical Woods*, 1st December, 1935 (No. 44), pages 26-30. The following excerpt gives added weight to the importance of the movement to introduce common sense into botanical nomenclature.

"Botanists continue to propose new species on the basis of size of leaves and fruits, length of petioles, angle of leaf bases, relative abundance of pubescence, and other minor features with only the haziest idea of their systematic worth and with no regard for the behaviour of plants in nature. Giving the rank of true species to mere tendencies of variations in response to edaphic or ecological conditions instead of designating them varieties, forms or mere states, helps no one and seriously interferes with the work of the xylogist, as well as the forester, ecologist, and all concerned with living plants. It is our duty to call these reckless botanists to account, and to make it clear that taxonomy is not a game but a serious effort to find a natural classification for plants."

It is not generally recognised how far-reaching is the influence of the ever-changing botanical nomenclature on scientific investigation as well as in commerce. A stabilised botanical nomenclature is of fundamental importance to all investigators, particularly those handling plant products.

Rapid changes in botanical nomenclature adversely affect the work of other investigators and, consequently, a very great disservice has been rendered to chemists and others engaged in the investigation of our native flora. That the influence is felt over a very wide range of interests is evinced from a publication which has just come under my notice. In an informative brochure issued by the Postmaster-General's Department, under date 19th December, 1935, dealing with the subject of selection and purchase of wooden poles, a matter of very great importance, attention is directed to the necessity for the adoption of correct nomenclature for pole timbers. It is pointed out that different species of timber are referred to by the one common name, as for example, Stringybark, and again the common or local name of the same species of timber may vary in different States, e.g. *E. regnans* is Mountain Ash in Victoria and Swampy Gum in Tasmania.

It is pointed out that the only certain way of preventing confusion caused by the mixture of common or local names at present in use in Australia is to cultivate the use of the botanical name in each case. This is particularly important in dealing with contracts, for it is the only way in which species of timber to be supplied can be definitely described and identified. How can engineers and foresters place any confidence in botanical names unless an attempt is made to obtain stability of nomenclature?

#### SANDALWOODS.

In discussing the subject of timber I am reminded of sandalwood, a tree which occurs in quantity in the arid regions of West and South Australia. It is a very valuable forest product which is exported in considerable quantities from Western Australia. Limited quantities are produced in South Australia and Queensland in accordance with the regulations and conditions operating under the Sandalwood Committee. The unstable condition of the market in China for sandalwood and the desirability of controlling the pulling of sandalwood necessitated the industry in Western and South Australia being placed under the control of the Sandalwood Export Committee in accordance

with the Sandalwood Act of 1930 and the amendment to it of 1933.

According to Western Australian authorities the sandalwood industry in Western Australia dates back to 1846, when the first record shows that four tons of wood, valued at £50, was exported. Until the establishment of the Mysore (India) monopoly for East Indian sandalwood, trade in sandalwood from Western Australia to other countries proceeded without any interference from the Government. Large tracts of forest were denuded of sandalwood and shipped away along the coast of Western Australia to Eastern markets. Sandalwood at the present time can only be pulled under licence, and these licences are only issued by the Sandalwood Export Committee when required to execute orders from China. Pullers of sandalwood in South Australia are paid £13 10s. per ton f.o.r. Port Adelaide, out of which they have to pay £1 per ton as royalty to the Government. According to the publication of H. R. Gray,<sup>4</sup> in normal times the annual export value of sandalwood sap-free logs is about £250,000. corresponding with an export value of about £30 per ton. This authority also states that this diminutive tree of straggling habit is the most valuable one, weight for weight, in Australia. As a result of departmental control in Western Australia of recent years the export has decreased considerably. For the year ended 30th June, 1935, the export value totalled £108,641, made up of the following quantities, viz.:

|                   |    |    | Cwt.         | Value.         |
|-------------------|----|----|--------------|----------------|
| Queensland        | .. | .. | 9,689        | £18,074        |
| South Australia   | .. | .. | 19,273       | £24,093        |
| Western Australia | .. | .. | 44,458       | £66,475        |
|                   |    |    | <hr/> 73,420 | <hr/> £108,641 |

The logs of sandalwood, free from sap, are exported to the East for incense purposes, whilst the roots and butts are used in the production of sandalwood oil. The oil is exported in comparatively large quantities for pharmaceutical purposes, but principally as a fixative for perfumes. Sandalwood oil is a very valuable forest product. The trade in this oil increased from 6,870 lbs.

<sup>4</sup> "Timber Supply, Consumption and Marketing", Fourth British Empire Conference (South Africa), 1935.

weight in 1921 to about 100,000 lbs. in 1930. Of recent years the trade has dropped to approximately 30,000 lbs. of oil per annum.

The Western Australian manufacturers are to be congratulated on the excellent quality of the oil produced, which is at least equal to the better known and well established East Indian sandalwood oil. Both these oils contain sesquiterpene alcohols to the extent of 90 to 95 per cent. Santalol is the principal alcohol in both oils.

Investigations into the chemistry of Western Australian sandalwood oil are of very great importance, and much work has already been accomplished and published in the Journal of this Society.<sup>5</sup> One of the most important chemical problems awaiting solution is the constitution of the several alcohols in the Western Australian oil.

As mentioned before,  $\beta$ -santalol is the principal alcohol, but there are other alcoholic bodies about which very little is known at the present time. These investigations are already in progress by the author, in collaboration with Professor J. L. Simonsen, F.R.S., of the University College of North Wales, Bangor, North Wales, and associates. It is anticipated that this work will be completed by the end of 1936. Meanwhile an account of the preliminary work which had to be undertaken has already been published.<sup>6</sup>

The oil from Western Australian sandalwood has suffered a great deal in competition with the East Indian oil on account of the unfair tactics adopted by overseas competitors in using differences in chemical composition and botanical nomenclature for trade purposes. The difficulties encountered in securing markets for Western Australian sandalwood oil in competition with the East Indian product are due in great measure to the action of the systematic botanists in repeatedly changing the botanical name of the sandalwood tree in Western Australia. First of all it was known as *Santalum spicatum* or *Santalum cygnorum*, then changed to *Fusanus spicatus*, and lastly to *Eucarya spicata*. The East Indian wood is known as *Santalum album*.

This is one of the most striking examples of the lack of common sense displayed by systematic botanists in dealing with the names of important economic trees. Even now

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<sup>5</sup> THIS JOURNAL, 1928, 62, pp. 60-71; 1932, 66, pp. 240-247.

<sup>6</sup> Journal of the Chemical Society, March, 1935, pp. 309-315.

the last designation, *Eucarya spicata*, is not accepted by some Australian botanists. Therefore, it will be fully appreciated that those marketing the East Indian product have not been slow to avail themselves of the botanical name of the Western Australian product for trade purposes. The Western Australian manufacturers are certainly to be commended for the manner in which they have been able to increase the santalol content of the oil from 40 to 45 per cent. in 1928 to about 75 per cent. at the present time.

Before leaving the subject of sandalwood I would like to direct attention to another potentially valuable tree, *Eremophila mitchelli*, which is widely distributed in the drier areas of New South Wales and Queensland, and known vernacularly as "Bastard" Sandalwood or Budda. It is a matter for regret that this small tree is exploited almost entirely for firewood, with a consequent loss of considerable quantities of essential oils which are present to the extent of 3 per cent. This essential oil has been thoroughly investigated<sup>7</sup> and its composition almost completely elucidated.

The oil was found to consist almost entirely of three crystalline substances: eremophilone, melting point 42°; 2-hydroxyeremophilone,  $C_{15}H_{22}O_2$ , m.p. 66°-67°; and 2-hydroxy-1 : 2-dihydroeremophilone,  $C_{15}H_{24}O_2$ , m.p. 102°-203°. These substances are of very great academic interest, and are the first naturally occurring sesquiterpene ketones and hydroxyketones to be found in nature.

The oil has been shown to possess marked fixative properties, but up to the present has not secured a market. No doubt the ramifications of the sandalwood industry have militated against its exploitation. Possibly it will come into its own when supplies of sandalwood in Western and South Australia become depleted. Under the name of "Rosewood" it has, however, in recent years been exported from Queensland to the East, where it is no doubt used for incense purposes as a substitute for genuine sandalwood.

#### EUCALYPTUS OIL.

The next most important forest product is eucalyptus oil. As mentioned before under the heading of Timber, eucalyptus oil was one of the first articles exported from

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<sup>7</sup> THIS JOURNAL, 1931, 66, pp. 420-433; *Journal of the Chemical Society*, 1932, pp. 2745-2759.

this country in 1788. Joseph Bosisto, C.M.G., a Victorian pharmacist, played a very important part in the establishment of the industry in Australia as far back as 1852. Acting on the suggestion of Baron von Mueller, the Government Botanist of Victoria, Bosisto undertook the investigation of the eucalyptus oils on a commercial basis. He commenced operations in a small rudely constructed still at Dandenong Creek, two miles out of Dandenong, Victoria, in 1852, using the leaves of *Eucalyptus amygdalina*, which grew profusely in that district. From that date to the present time eucalyptus oil has excited considerable attention, not only in Australia, but in all parts of the world. The annual export of oil has reached approximately 100,000 gallons, valued at £40,000 to £45,000, a not insignificant minor source of national income. Efforts have been made to increase the exports to about 200,000 gallons per annum, but so far with little success, due in great measure to competition from oil produced in Spain and Japan. Apparently the very low prices ruling for eucalyptus oil in Australia during recent years has practically eliminated Spain as a competitor, for it is understood that Spanish distillers are appealing to their government for assistance.

The position in connection with the competition with Japan is very difficult to combat. In the first place the oil is sold as Formosan eucalyptus oil, although it is not distilled from a eucalypt, but is essentially a by-product rich in cineol, produced by the refining of the oil of camphor produced in Formosa.

So far as the chemistry is concerned no plant product has been investigated so exhaustively as the essential oils from the eucalypts. The first investigation of eucalyptus oils was undertaken by M. Cloez in 1870 upon the oil of *Eucalyptus globulus*. This species had been successfully cultivated in many parts of the world, although the young shoots of the trees grown in Paris did not withstand the frost. It was due to this circumstance that Cloez was led to investigate the essential oil obtained from the leaves. Further investigations were undertaken by E. Jahns and by M. R. Voiry in 1888. It was a few years later that the classic investigations of Baker and Smith were initiated, and, as you are aware, these have been continued by their successors with unabated vigour right up to the present time.

There was a definite decline in the exports of eucalyptus oils until it was shown, in 1920, that synthetic thymol and menthol could be produced from the oil of *Eucalyptus dives*. This gave an immediate fillip to the utilisation of that particular species, with the result, as mentioned before, that the exports have maintained a fairly constant level of 100,000 gallons per annum.

Despite competition from other raw materials, piperitone from *Eucalyptus dives* is still sought after by British, Continental and American manufacturers as a basic material for the manufacture of synthetic thymol and menthol.

Apart from the question of increasing our exports, a phase of the matter which has not received the attention it deserves is the continuity of supplies of raw materials to meet any unprecedented demand. I am doubtful if the existing areas of the commercial species of eucalypts would be sufficient to maintain continuity of supply if our exports of oil were doubled. There is a steadily increasing demand for the oil of *Eucalyptus Australiana*, which contains a minimum content of about 70 per cent. cineol, with a delightfully refreshing aroma due to a blending with  $\alpha$ -terpineol and cineol. Unfortunately the areas of country upon which the species abounds is being rapidly cleared for grazing purposes, and, consequently, there is a grave danger of the extinction of this species.

Similar remarks apply to the "Broadleaved Pepper-mint", *Eucalyptus dives*, and it is suggested that those interested in the exploitation of these two species should co-operate with the Forestry Commission of New South Wales in reafforesting, where possible, some of the Crown lands upon which the species is sparsely distributed, or take steps to encourage its natural regeneration. It is a very difficult problem, however, when private property is concerned. Excellent areas of eucalyptus oil-producing country are being rapidly cleared in the Bathurst and Tumbarumba districts of New South Wales, and in many of these areas it would be advisable for the country to be maintained for oil production. There is evidence that if the areas are cleared entirely of these trees, altogether apart from the injury being done to the exploitation of a natural product, there is the graver problem of erosion. It is imperative, therefore, that something should be done to conserve some of these areas around the Oberon and Tumbarumba districts. If the areas were simply being

cleared of big trees and maintained for oil production it would be a different problem, but there is abundant evidence that after cutting the trees for eucalyptus oil the stumps are poisoned, with the result that the trees are extinguished for all times.

One of the most important results of investigations into the chemistry of the eucalypts of recent years has been the discovery of the physiological forms, i.e. forms or varieties of well-known species indistinguishable from one another on morphological grounds, but which are found to yield essential oils of diverse chemical composition.<sup>8</sup> These investigations have not only been the means of opening up new areas of country for exploitation, but have brought in their train very important problems in genetics. The occurrence of these physiological forms has exerted considerable influence on the economic exploitation of many species of eucalypts and other essential oil yielding plants of commercial value. It is hoped that arrangements may be made in the near future for the investigation of these physiological forms to be continued by chemists working in conjunction with a geneticist.

The comparatively high germicidal efficiency of certain eucalyptus oils has given a fillip to the economic utilisation of the residues left after their refining for medicinal purposes. There is scope for further investigation in the development of a special technique whereby concentrated emulsions can be so manufactured that they will possess Rideal-Walker coefficients equivalent to the dilute dispersions. For a discussion on this important phase of preparing and testing disinfectants from eucalyptus oils readers are referred to a series of papers published in the Journal and Proceedings of this Society.<sup>9</sup>

Another development which might be expected is a greater utilisation of some of the components of eucalyptus oils such as australol, cuminal, phellandral and 1-4-isopropyl- $\Delta^2$ -cyclohexenone.

#### TEA TREE OIL.

Investigations into the germicidal properties of essential oils has led to a very remarkable economic development,

<sup>8</sup> THIS JOURNAL, 1927, 61, pp. 54-67; 1928, 62, pp. 82-78; 1929, 63, pp. 79-84; 1932, 66, pp. 181-193; 1933, 67, pp. 351-363; 1935, 69, pp. 111-22.

<sup>9</sup> THIS JOURNAL, 1922, 56, pp. 219-226; 1923, 57, pp. 80-89, 211-215; 1924, 58, pp. 117-123; 1925, 59, pp. 346-350.



and that is the commercial utilisation of the leaves of the "Narrowleaf" Tea Tree, *Melaleuca alternifolia*, which occurs in such abundance in the swampy country between the Richmond and Clarence Rivers of New South Wales. This particular "Tea Tree" has been the bugbear of dairy farmers of the North Coast for many years, since, short of grubbing out, it resists extermination. Its reproductive properties after repeated cutting back are truly remarkable. The great value of the oil in surgical and dental practice has enabled owners of these swampy regions to derive revenue from otherwise totally unusable lands.

*Melaleuca alternifolia* is a tree which, popularly speaking, likes to have its feet in water. It is noteworthy that on sloping undulating ground above the swamps the oil varies in chemical composition. The oil obtained in a yield of 1 to 1.5 per cent. from the leaves in terminal branchlets is non-toxic, non-irritating, and non-poisonous, and its relatively high germicidal efficiency when compared with carbolic acid has led to its commercial exploitation by a well-known Australian company. I have, in the course of many popular lectures, brought under notice some of the complaints which have responded in a very remarkable way to treatment by this oil. Its success depends, in very great measure, upon its ability to dissolve pus, thus making available sterile tissue which readily heals. The value of the oil does not depend upon one particular constituent, but upon a unique natural blend consisting of *a* and *y* terpinene, cymene, cineol (8 per cent.), *d*-*a*-pinene,  $\Delta$ -terpinenol-4, sesquiterpenes, etc. The botany and chemistry of the essential oil of this tree were first described in the Journal and Proceedings of this Society,<sup>10</sup> and in Bulletin No. 14, Part I, published by the Sydney Technological Museum in 1934. It is worth noting that although certain essential oils have been favoured on account of their content of cineol, as for example eucalyptus oil, it has been found necessary to limit the amount of cineol in tea tree oil to under 10 per cent. The normal commercial distillate of *Melaleuca alternifolia* contains less than 5 per cent. of cineol. The present annual production is approximately 1,600 gallons. It is of general interest to record that the production of this quantity of oil requires over 25,000 acres of well stocked country and

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<sup>10</sup> THIS JOURNAL, 1922, 56, pp. 219-226; 1925, 59, pp. 346-350.

the cutting of approximately 640 tons of leaves and terminal branchlets.

Whilst on the subject of "Tea Tree" oil I would like to direct attention to another tea tree called *Leptospermum citratum*. The essential oil of this "Lemon-scented" Tea Tree was first brought under notice in the Journal and Proceedings of this Society.<sup>11</sup> During the period which has elapsed since the publication of the chemical composition of its essential oil much experimental work has been carried out in connection with the cultivation of this tea tree for economic purposes. It was realised soon after the composition of the essential oil had been revealed that any demand for the oil could not be met as insufficient material was available.

The tree has so far been observed in comparatively small areas at Copmanhurst and surrounding districts (near Grafton), N.S.W., and at Springbrook and Palmwood, Queensland.

A great deal of work on its experimental cultivation has been carried out by members of the Society, and a summary of the results up to 1935 was published in a bulletin recently issued by the Sydney Technological Museum.<sup>12</sup>

Despite the captious criticism which has been levelled at the economic exploitation of this tree, based principally on the relation of its chemical composition with cheaper sources of raw material in other parts of the world, there is every likelihood of the oil finding a good market in Australia. The reasons upon which this optimistic view is based are clearly indicated in the publication issued by the Sydney Technological Museum.

#### SUNDRY ESSENTIAL OILS.

The essential oil from the sawdust and waste wood of the well-known Huon Pine of Tasmania, *Dacrydium Franklinii*, is of some commercial importance. The wood has been utilised for many years, and is noted for its white-ant- and borer-resistant properties, doubtlessly due to the large amount of oil which it contains, usually from 3 to 5 per cent. on the weight of the wood.

The oil, which is of a pale yellow colour, and heavier than water, contains from 90 to 95 per cent. of methyl

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<sup>11</sup> THIS JOURNAL, 1918, 52, pp. 175-180.

<sup>12</sup> Bulletin No. 14, Part II, "Australian Tea Trees of Economic Value".

eugenol.<sup>13</sup> It possesses a Rideal-Walker coefficient of 10 to 12. It has been found of value for the treatment of perionychia, tinea, cuts and wounds, and as a preservative in casein preparations. About 1,200 gallons of oil are produced annually.

Another plant of considerable popular interest which has been exploited for its delightful perfume is *Boronia megastigma*, the Brown Boronia of Western Australia. *Boronia megastigma* is a shrub about six feet in height, found in the swampy situations in the south-west of Western Australia. Girls and youths are employed as pickers of the bloom from plants which are gathered from Crown lands in the extreme south-west of Western Australia as, for example, such districts as Mount Barker, Albany, Bridgetown, and Greenbushes. The blossom is removed with specially made combs constructed from inverted horseshoe nails attached to a container. Pickers will gather, in good country, about three pounds of blossom per hour. The price of the blossom varies from 1s. 6d. to 2s. per pound, including royalties.

So far as I am aware this is the only boronia which is exploited for commercial purposes. This is readily understandable, for no other boronia occurs so abundantly as *Boronia megastigma*. The flowers are used for the production of a concrete otto, which is prepared by two leading essential oil producers in Western Australia. The concrete otto has only been produced for a comparatively few years, and it is computed that about 300 lbs. weight of concrete from 75,000 lbs. of blossom has been produced. It is interesting to note that very limited quantities are exported, as most of it is used in Australia, where it forms the basis of some beautiful creations of the perfumer's art. The chemical composition of the concrete otto was investigated by me in 1927.<sup>14</sup>

Australia is extraordinarily rich in essential oil-yielding plants. A very large number have been investigated, as a perusal of the pages of this Journal will reveal, particularly during the period 1920-1930.

The investigations have concerned such important genera as *Leptospermum*, *Melaleuca*, *Boronia*, *Prostanthera*, *Zieria*, etc. Only a comparatively few have as yet been found worthy of commercial exploitation. The reasons

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<sup>13</sup> *Perfumery and Essential Oil Record*, 1926, pp. 508-509.

<sup>14</sup> *Journal of the Royal Society of Western Australia*, 1927, 14.

are not far to seek. Firstly the composition of many does not differ materially from well-known and established oils obtained from more abundant and cheaper sources, secondly the yield of oil and limited quantities available in their native habitat precludes commercial exploitation. Others, of course, are noted for their unique composition. Some of these more important and interesting substances provide a starting point for the synthesis of other compounds or are a source of raw material for the manufacture of important synthetic products.

Some of the most remarkable substances isolated from plant products have been obtained from Australian essential oils, such as eudesmol, piperitone, 1-4-isopropyl- $\Delta^2$ , cyclohexanone, angustione, dehydroangustione, eremophilone, 2-hydroxyeremophilone and 2-hydroxy-1:2-dihydroeremophilone.

It is not within the power of any one individual to forecast the future prospects of any of the Australian essential oils which have been investigated. It is simply a question of time, and dependent to a great measure upon the population which this country might eventually carry, and also upon the exhaustion of supplies of various commercial oils from overseas sources.

#### TAN BARKS.

Australia is very rich in tannin-bearing plants, the most important of which is the wattle bark, obtained from the different species of *Acacia*. Wattle bark is the principal tanning agent used by Australian tanners. Wattle tannage produces a pliable mellow product of good colour, which can be converted into kip, bag, strap, haversack, and sole leather. The principal species are *Acacia pycnantha* and *Acacia mollissima*. The former occurs principally in South Australia, Victoria, and south-western New South Wales. *Acacia mollissima*, commonly called the Black Wattle, the air-dried bark of which contains more than half its weight of tannin, is strongly recommended for cultivation. It, of course, occurs widely distributed throughout the southern district of New South Wales, and is collected for commercial purposes in such localities as Bateman's Bay, etc.

Unfortunately the story of the wattle bark industry is a very sad one for Australia. About fifty years ago South Africa established wattle bark plantations from seed collected in South Australia. Today 300,000 acres are

under plantation in that colony. Tan bark and tannin extract to the value of £1,000,000 are exported annually. Mine props bring in an additional £500,000 per annum, and the industry ranks fourth in the Union's agricultural industry.

The treeless grassy highlands of Natal are specially suitable for wattle culture, and the tree can, therefore, be grown in rows and economically tended to, while the necessary bark sheds and appurtenances can be placed in the most advantageous position. Moreover, there is an abundance of cheap and efficient native labour available for employment on the plantations.

Although there is an import duty of £3 per ton, it does not seem to have afforded very great encouragement for the cultivation of the wattle in Australia. The prevailing rate of exchange has greatly assisted the industry during the past ten years, as is evident from the following statistics, which are very illuminating, viz. :

| Year.   | IMPORTS.           |             | EXPORTS.           |             |
|---------|--------------------|-------------|--------------------|-------------|
|         | Quantity.<br>Cwts. | Value.<br>£ | Quantity.<br>Cwts. | Value.<br>£ |
| 1925-26 | .. 44,372          | 21,498      | 6,448              | 3,818       |
| 1926-27 | .. 57,302          | 27,680      | 5,935              | 4,010       |
| 1927-28 | .. 5,114           | 2,633       | 46,549             | 33,511      |
| 1928-29 | .. 1,562           | 755         | 56,804             | 33,798      |
| 1929-30 | .. 1,926           | 950         | 70,040             | 38,604      |
| 1930-31 | .. 596             | 266         | 70,357             | 32,234      |
| 1931-32 | .. 21              | 13          | 89,061             | 72,289      |
| 1932-33 | .. 200             | 101         | 76,594             | 35,892      |

The principal bark exported is mallet bark from Western Australia, which constitutes about 60 per cent. of the total exports. According to the Commonwealth Statistician, taking an average for the past five years, Germany has taken 42 per cent. of the total exports, New Zealand 36 per cent., and the Netherlands 14 per cent.

The excess of exports over imports during the past six years amounted to 3,600 tons, valued at approximately £37,000, Western Australia and South Australia being the principal exporting States. The total production of tan barks in Australia is estimated at 27,000 tons.

The cultivation of wattle for the production of bark cannot be too strongly recommended, and unless early steps are taken to retrieve the position it looks as if the industry has passed to South Africa for all time. The South Africans have been studying the position very

thoroughly, so much so that they are now planting from selected trees. It has been found that certain trees have thicker bark than others, and, as it has been shown that the thicker the bark the greater the concentration of tannin, it is perfectly obvious that it is only a matter of time when their plantations will consist solely of these selected trees very rich in tannin.

#### GUMS AND RESINS.

Australia is not rich in water-soluble gums. The conflict between Italy and Abyssinia has resulted in numerous enquiries for supplies of commercial Acacia gum from Australian wattles. Unfortunately there has been no systematic collection, for in the past no encouragement has been offered on account of the abundant supplies available in the Sudan and the cheaper labour cost of collecting the gum in that country. It is evident that considerable difficulty would be experienced in collecting the quantity required, as the total Australian consumption is approximately 500 tons, valued at £17,000.

Australia is also comparatively weak in resins, the most important and best known being Grass Tree resin (*Xanthorrhæa* sp.). There is a good deal of information about this resin scattered throughout the literature, but a short account of the distribution, properties and value of the resin is given in Bulletin No. 16, issued by the Sydney Technological Museum.

These Grass Trees, sometimes called "Blackboys", especially in Western Australia, or yaccas or yackas, are widely distributed throughout the Commonwealth of Australia. They are characterised by their bunches of grass-like leaves growing at the top of an elongated trunk like a palm. Grass trees are found only in Australia, and belong to the genus *Xanthorrhæa*, which comprises a number of species of tree-like shrubs belonging to the lily family. The trunks consist of the old leaf bases, in which the resin is deposited, being either yellow or red in colour, according to the particular species. The yields vary according to the species from which obtained, but the following represent fair average returns, viz.:

|  | Per tree.  |
|--|------------|
| Yellow Resin ( <i>Xanthorrhæa hastilis</i> ), N.S.W. | 3 lbs.     |
| Red Resin ( <i>X. tateana</i> ), South Australia ..  | 37 "       |
| Red Resin ( <i>X. preissii</i> ) .. .. .             | 42 to 67 " |

The yields clearly indicate why the industry is of negligible value in New South Wales. The present price of the grass tree resin (red) is £6 per ton, f.o.b. Adelaide. The total production for the year ended 30th June, 1935, was 45,257 cwts., of which 44,098 cwts. were obtained from Kangaroo Island, South Australia.

There is an ever-increasing demand in New South Wales for grass tree resin for certain types of stove and wood polishes and floor stains.

It is rather remarkable that despite the number of investigations which have been conducted on the chemistry of grass tree resin, we know very little about the actual constituents of this unique resin. A critical examination using modern methods is urgently needed. I feel that an exhaustive chemical investigation would afford not only much useful knowledge concerning its composition, but provide some useful information which would assist in an increased technical application of the resin, as for example, in the plastic industry.

#### STARCH.

The two most important natural sources of starch in Australia are :

- (a) The Burrawang Palm (*Macrozamia spiralis*).
- (b) The "Bunya Bunya" Pine (*Araucaria Bidavilli*).

The chemistry of the Burrawang Palm was investigated by Dr. J. M. Petrie in 1920.<sup>15</sup> Dr. J. M. Petrie, in his paper, mentions that *Macrozamia spiralis* was first examined chemically by Norrie, a pharmacist of William Street, Sydney. His report is published in a short paper on *Macrozamia spiralis* by Dr. F. Milford.<sup>16</sup> The preparation and edible properties of the "arrowroot" from the Burrawang Palm are interestingly described. The seed of the "Bunya Bunya" was subjected to chemical examination by F. R. Morrison in 1924.<sup>17</sup>

The seed of the "Bunya Bunya" was found to contain about 66 per cent. starch, and this yield compares favourably with the yields obtained from many commercial sources of starch. There is, however, some doubt about the quantity of seeds available, and whether they could be collected without difficulty, and it would appear that it is

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<sup>15</sup> THIS JOURNAL, 45, pp. 424-442.

<sup>16</sup> THIS JOURNAL, 1876, 10, pp. 295-297.

<sup>17</sup> THIS JOURNAL, 1924, 58, pp. 234-239.

not a promising commercial source of starch at the present time.

On the other hand the very attractive Burrawang Palm, which occurs so plentifully in the far south coast district of New South Wales, particularly around Bateman's Bay, was utilised some years ago for its starch content. Apparently it was a commercial success for some time, but a number of technical difficulties which subsequently arose forced the abandonment of the project. A brief account of the distribution of the Burrawang Palm and some notes about the properties of the starch are worthy of record.

The main belt of Burrawang Palm occurs on the south coast between Milton and the Victorian border for a distance of approximately 100 to 120 miles. The palm belt varies in width from about four miles to twenty miles, and in some gullies it is so thick and the palms so big that it is impossible to travel through them, even on horseback.

In 1921 a company was formed to manufacture starch from this palm. The structure of the palm is very similar to that of other bulbous palms. The factory which I visited in 1921 was situated at Shallow Crossing, about twelve or thirteen miles up the Clyde River from Nelligen. This factory utilised only the central part of the palm (which contains approximately 35 per cent. of starch), though there is no reason why the outer section should not also be used, as this contains approximately 25 per cent. The inner portion gave a commercial yield of 28 per cent. to 30 per cent. of starch, the balance being allowed to remain in the pith, from which it was subsequently removed and utilised for the preparation of commercial adhesive paste.

Burrawang Palm starch, when subjected to a microscopic examination, revealed some interesting features. Rice starch, which is always favoured for laundry purposes, consists of very fine grains. Maize starch, on the other hand, is considerably coarser. The Burrawang Palm starch consists of various sizes of grains varying from very fine particles similar to rice starch. The practical significance of this is apparent from reports received from a number of laundries where Burrawang starch was submitted for test purposes. They reported that the starch from this palm was 50 to 70 per cent. stronger than any other starch, using the best rice starch for comparative purposes.



The explanation is comparatively simple. The particles of starch being graded, the very fine ones are able to penetrate into the body of the fabric, while the coarser ones remain on the surface. These, when converted into other compounds by the action of a hot iron, give it a strength just where it is needed in the fabric.

#### FIXED OILS.

Australia is very poorly supplied with plants yielding fixed oils. Fixed oils have been obtained, and their chemical composition elucidated, from *Macadamia ternifolia* and *Macadamia integrifolia*, two closely allied trees yielding the Australian nut of commerce. These two trees are natives of New South Wales and Queensland, and although in their native habitat in the brush they are tall trees with thin bark, due to their fight for light, they become very handsome foliaceous trees when planted in the open. The few trees which were left in the North Coast district of New South Wales when the land was cleared of vegetation for banana growing and farming developed into handsome trees up to thirty-five feet high, with a spread of thirty feet in diameter. Both trees are renowned for the highly nutritious dessert nut of excellent flavour, and for the reputation it has achieved as the hardest nut in the world to crack. These nuts are obtained in yields varying from 30 lbs. to 100 lbs. per tree, according to age, and are known at present as the Australian Nut. Until by common consent a change was made a few years ago, they were known under a variety of vernacular names. The most common were Queensland, Bush and Popple Nut, whilst the Australian aborigines called them "Kindal Kindal".

The Australian Nut is a highly esteemed dessert nut, but the market is restricted to some extent because of the difficulty in cracking the shell with the ordinary nut-crackers. A thin shelled nut has been obtained which can be cracked readily with the ordinary nut-crackers. This opens up an interesting problem in horticulture, for propagation from selected trees should solve the very difficult problem of cracking the shells.

There is an excellent market abroad, especially in America, for the kernel for various confections and nut products. The present demand is such that it could not be met, as practically the whole of the annual production (twenty tons) is consumed in Australia.

There are a number of plantations on the north coast of New South Wales, particularly around Lismore and Murwillumbah, but there is need for their extension. Nevertheless, many residents of the North Coast are alive to the value of this tree, and there are probably close on 10,000 *Macadamia* trees under cultivation. The tree does not bear until the fifth year, whilst good crops are not obtained until the seventh year. It can be most profitably grown as a breakwind or in conjunction with bananas or some other quick return crop. The kernels contain 72 per cent. of oil, which is practically water white, and equal to the best grades of olive or almond oil, which it closely resembles in chemical composition.

It is too good a table nut to be used for conversion into oil, but in the preparation of nuts for table use there is sure to be a certain quantity of damaged ones, and it is these that should yield a profitable return if converted into oil. A bulletin dealing with the cultivation and exploitation of the Australian Nut, together with particulars of the chemistry of the fixed oil, has just been issued by the Sydney Technological Museum.<sup>18</sup>

The fixed oil from the seed of the well-known kurrajong tree (*Brachychiton populneum*)<sup>19</sup> is the only other important oil to command notice.

The kurrajong is a widely distributed shade and fodder tree, but the quantity of seed produced annually would not warrant economic exploitation, as the chemical composition of the oil is not of unusual interest.

#### ALKALOIDS.

Australia is relatively weak in plants yielding alkaloids of commercial importance. Many Australian plants contain alkaloidal substances, but usually they are present in insufficient quantity or are of negligible commercial importance.

In the natural order Solonaceæ<sup>20</sup> we have two *Duboisias* native to New South Wales and Queensland. Only one is of commercial interest, and that is *Duboisia myoporoides*, which occurs along the eastern coast of New South Wales and Queensland. The leaves contain hyoscyamine, nor-

<sup>18</sup> Bulletin No. 20, "The Cultivation and Exploitation of the Australian Nut".

<sup>19</sup> THIS JOURNAL, 1925, 59, pp. 267-275.

<sup>20</sup> *Proceedings Linnean Society of New South Wales*, 1917, 42.

hyoscyamine and scopolamine, alkaloids of the atropine group.

There have been numerous enquiries for supplies of *Duboisia myoporoides* from Europe, but an extensive business has not developed, although there is a considerable demand for natural sources of atropine alkaloids. There does not appear to be any great difficulty in supplying the required leaves, but complaints have been received concerning the variable content of hyoscyamine.

The chemistry of the leaves of *Duboisia myoporoides* was worked out by Dr. Petrie. There is certainly need for a critical investigation of the alkaloidal content of leaves of *Duboisia myoporoides*, particularly concerning the age of the leaves, climatic, soil, and other conditions operating, whereby the alkaloid varies both in content and chemical composition from time to time. The investigation is warranted, as there is a demand for approximately 100 tons of leaves per annum.

I trust that the foregoing review of the forest products of Australia will be of some interest to the readers of this Journal. I trust also that it will inspire the people of Australia with a greater appreciation of the forest wealth of Australia and its potentialities.

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## THE AEROPLANE IN THE SERVICE OF GEOLOGY.\*

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With Plates I and II and two text-figures.

I desire to thank the Council of the Royal Society of New South Wales for the signal honour they have conferred on me in appointing me to deliver the Clarke Memorial Lecture for 1936.

It is well to pause now and then in our ever increasing rush and bustle to consider the foundations upon which our scientific beliefs rest, and to remember the men who laid those foundations firm and strong for us of a later and more favoured generation to build upon. For we are favoured, scientifically at all events. We have not only the solid facts obtained for us by our predecessors, but we have those facts winnowed from the uncertain speculations with which they were inevitably associated. Further, we have new angles of vision, not vouchsafed to them, and new weapons of attack upon problems which baffled them, and it is for us to try to make as good use of our opportunities as did the pioneers of their more limited ones.

Certainly the pioneers had some advantages which we do not possess. They had a virgin field, as yet entirely unexploited. Anywhere they went their observations were new, and even the simplest and most obvious facts were to be recorded for the first time. They had the "licence of the pioneer" to carve their own tracks through the wilderness, to a large extent without regard to their most suitable location; in other words, they were allowed breadth of treatment, and were not necessarily limited to absolute accuracy in minor matters of detail, which we, their successors, must inevitably take strictly into account. I think this aspect is often not sufficiently realised by the present generation, and quite unnecessary criticisms of early work are made in consequence.

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\* Clarke Memorial Lecture delivered to the Royal Society of New South Wales, March 20, 1936.

May I be permitted to digress slightly in illustration. It is commonly stated in popular works today that Einstein has disproved the Newtonian Laws of Gravitation. This is not the case at all. Newton's equations are just as sound as ever *within the limits to which they are applicable*. What Einstein has done is to add terms containing higher powers of the variables. Only in limiting cases of special character are these higher terms appreciable in effect. In ordinary celestial mechanics, as typified in the preparation of the Nautical Almanac, for instance, the Newtonian equations are as sound as ever, and suffice for the utmost refinement of navigation.

Australia has had many great geologists, and tonight we honour the memory of one of the greatest of them, Rev. W. B. Clarke. It is unnecessary for me again to sketch his scientific career to you. This has been done more than once in the volumes of our Society. I propose to honour his memory by drawing a contrast between his opportunities for research and those which we enjoy today as a means of impressing on you the magnificence of the work which he did in the face of so many and such great obstacles. I propose to treat especially of one aspect, namely the contribution made by the application of the aeroplane to the study of geology.

In Clarke's day the world moved in a leisurely fashion, and time was a factor of minor importance. The railway system of the State was embryonic, and travel was almost entirely by means of horses. With such limited facilities Clarke covered the colony of New South Wales almost from corner to corner, and, wherever he went, he made profound and accurate observations, which have served, ever since, as the guide and basis of subsequent research. It is only to be expected that many of his conclusions have had to be modified as a result of more concentrated, more protracted and better equipped investigations; but I think we may say that, in most instances, the corrections are elaborations rather than erasures.

Even I, now amongst the "old brigade" of the members of the Society, never knew personally the pioneer whose memory we honour, and even I, in my younger days, possessed advantages of transport and equipment undreamt of by him. We, the "old fellows" of today, had as youngsters a much extended railway system, and most of us travelled thousands of miles by bicycle, with speed, mobility and economy quite unknown to the pioneer.

You younger people, our fortunate successors in the field, disdain our vaunted superiority. You use the railway occasionally for attendance at interstate conferences; a journey to Perth, even, being regarded as a mere suburban trip. The geologist's bicycle is relegated to the museum, many of you have never been astride of horse or camel, and every one of you handles a motor car with perfect confidence and *sang froid*. Yet even you are at the threshold of still another era. The aeroplane has already proved its advantages, and even we "old fellows" have been able to glimpse something of what it is going to mean to you youngsters. We look forward with confidence to still other developments, giving still greater speed, stability and simplicity of handling, to the hovering plane and to other advantages which we ourselves will never experience, and we expect you to do better than we have done in consequence.

To many people even now that the technique is becoming somewhat common, the idea of doing geology by means of an aeroplane suggests the height of absurdity, and it is not inappropriate, at the dawn of the new era, to attempt to place before you some facts in relation to this technique. I am sure that the great men of the past in the geological investigation of our country would have been the first to realise both the advantages and the limitations of the method, and W. B. Clarke himself would have taken full advantage of it had it been available to him.

To most people geology means the study of the rocks composing the earth's surface, and it is on this inaccurate and misleading definition that opposition to the use of the aeroplane is founded. The study of the rocks is only one of the aims of geology. Much wider in scope, and of much greater ultimate importance is the delineation of the fabric and structure of the earth and the inference therefrom of the historical development of the earth itself.

So far as the limited conception is concerned, namely the study of earth materials, the sceptics are perfectly right. An observer thousands of feet above the ground travelling at a speed of over 100 miles an hour has no possible chance of detailed inspection of the rocks themselves, and can obtain no inkling of their fossil or mineral contents. This phase of geology can be studied in one way, and by one means of transport only. In the past, in the present and throughout the future the earnest geologist must do a large part of his travelling *per boot*. There is no possible

substitute for detailed investigation of the materials of the earth. The hammer and lens must be applied in the investigation of rocks and fossils, and the dolly pot and dish in the search for economic minerals. The introduction of motor car, aeroplane and future improvements in methods of transport can never absolve the geologist from the duty of carrying out these intimate investigations on the spot. The new methods are in extension of, and not in substitution for the time honoured routine of geological investigation. I wish to dispose of this fallacious objection very definitely and finally at this stage.

We should, however, be little, if anything, wiser if our researches were limited to observations in material geology. It is only by determining the mutual relations of the formations with which we have to deal and their bearing on geological history that the full value of the work becomes apparent.

The super-man in the geological world *may* be able to obtain an ensemble impression, leading to a complete and final explanation of every phase of the problem in a casual examination of an area; but most of us are compelled to extend our observations over longer periods, and to utilise every chance of picking up crumbs of knowledge in order that we may be able to make even a partial contribution to the sum total of geological knowledge.

The eye of an observer is so little raised above the ground level that, even in clear country, his circle of observation is limited to a radius of about twenty or thirty yards. Beyond that distance objects are so foreshortened that their mutual relationships become more and more obscure as the distance increases. This disability is overcome by constant change in the point of view, in other words, by making a *traverse* of the area under investigation, so that all parts of it are brought successively within the range of clear vision. This type of *survey* is a tedious business, and all but the few individuals, highly favoured by nature with specially retentive memories and special "bumps" of locality, are unable to orient and relate their observations without adventitious aids.

Hence the first aim of an ordinary geological survey is the preparation of a geological map, that is a representation, on a reduced but uniform scale, of all the essential facts of observation. When suitable conventions have been evolved, such a geological map makes available, not only to the observer himself but to all other adequately

trained persons also, the distribution and relationships of the *observed* geological details. Seen as one entity, and not piecemeal as the observations are necessarily made in the field itself, an ensemble impression is obtained, and mutual relationships are brought to light whose existence was not even suspected as the work progressed.

Such a map is essentially a two-dimensional representation of the surface geology of the area. If the topographic relief is strongly accentuated its effects in the vertical direction can be indicated on the map by the insertion of contour lines or other suitable convention. In any case, however, the application of perfectly straightforward, if somewhat complicated geometrical processes of analysis, makes it possible to determine, with a high degree of probability, the behaviour of the individual geological units in depth as well as in length and breadth. In this way, by means of suitably placed and suitably constructed *geological sections*, it is possible to convert the observed two-dimensional plan into a reasoned three-dimensional representation of structure. Naturally, since a geological section is an extrapolation, its credibility decreases as its departure from the realm of direct observation increases. This fact must always be kept clearly in view, and it must be remembered that a geological section is one man's reasoned interpretation of observed data, and that other persons, using different criteria for the extrapolation, may arrive at different conclusions.

Returning now to the observational realm, that is to the geological map, we have to consider how best the field geologist can be aided in the accumulation of his facts of observation, and in his graphical representation of them.

Every field geologist is conscious of the urge to obtain as nearly as possible a bird's-eye view of the ground on which he is working, and we "old fellows" have mostly had to be content with climbing the most precipitous hills we could find in the neighbourhood, or with climbing trees. Even from such vantage points the increased range of vision obtained has been found to be of the utmost importance, and most of us realise that we have obtained impressions in this way which have extended our knowledge, and corrected wrong ideas derived from the *too* intimate study of local details. We have been conscious of a longing to be able to borrow the wings of a bird so that we might obtain a true orthographic projection of our entire



area to replace our view at grazing incidence which was the best we could do under the then existing circumstances.

Let us take a simple illustration. Let us imagine an ant, endowed with human intelligence, crawling over a figured carpet. It realises that there is regularity and design in the variations in colour which it senses. It sets to work to survey the variations, and produces a map of them on small scale, so that it can visualise the entire plan. Using the map, it can place itself at any desired point in the pattern in order to make more intensive investigation of the details at that point.

If, however, our ant develops wings, it can soar above the floor and, looking down, can appreciate in a single glance the full details of the design. Even without the tedious work of minute representation of the features it can go immediately and with full confidence to any point at which objects of special interest appear, with full knowledge of the relationship between the details at this point and the purpose of the whole design.

The introduction of the aeroplane has conferred upon the geologist this same facility, and he is now able to *supplement* (mark the emphasis) his ground observations by means of a more extended bird's-eye impression of the whole structural pattern of the area.

The new point of view brings with it enormous advantages which have only to be experienced to be appreciated. There flashes into one's vision the entire structure pattern of the area. The continuity of persistent horizons which the geologist has followed laboriously and mapped on the ground becomes as clear as are the coloured lines by means of which such horizons are delineated on the completed geological map, and a feeling of confidence and satisfaction is engendered when it is found that the mapping has been accurate and adequate.

On the other hand there can rarely, if ever, be undertaken a flight over an area previously mapped by the observer which will not reveal an enormous amount of available detail entirely missed during the ground survey, if, indeed, there are not brought to light cases of actual error in representation and inference. Rock outcrops are rarely continuous over considerable lengths. Mostly they take the form of small and discontinuous patches of weathered rock material to a great extent hidden under soil and vegetation. In such circumstances it calls for a high degree of skill and experience to select and sort out the

confusing details so as to make a consistent and intelligible picture. In the aerial view soil differences, inappreciable on the ground, but obviously reflecting underlying rock variations, reveal details of sub-surface structure inaccessible to and unappreciated by the ground geologist.

Particularly where there is either one thick bed of rock of a certain type or, still more, where there are several bands of generally similar character, the piecemeal operation of mapping on the ground may lead to grave errors of correlation which can be detected only when the whole expanse is viewed from above as a unit. Under such conditions characters, such as slight differences in colour and reflecting power, or distribution of vegetation, quite inappreciable at grazing incidence of vision, become conspicuous, and it is realised that likes have been separated and unlikes grouped in error.

It must not be assumed by any means that ability to carry out aerial geological observations comes immediately and by instinct. This is definitely not the case. There are probably few people who will be unconscious of some sort of thrill, mingled with more or less apprehension, the first time they "take to the air". The unfamiliarity of the environment alone is sufficient to interfere with that detachment which is essential for the best type of scientific observation. In addition, there is a complete unfamiliarity with the aspect of familiar objects as seen from the air, and a considerable amount of experience is required before one can begin to recognise even the most ordinary landmarks.

This is due partly to the "change in dimensions" and partly to the unaccustomed speed of translation.

On the ground impressions of vertical height are not only important, but exaggerated. The horizontal distances we traverse in our ordinary affairs are large in comparison with our vertical movements. One thinks little of walking a couple of miles before breakfast, but a climb of less than one-tenth as much, say 1,000 feet, would be claimed and acclaimed as a notable feat at such a time of day. We are essentially two-dimensional animals. Travelling across a plain, a church steeple or a windmill is a landmark from afar, while a precipitous hill is known far and wide.

From moderate heights in the air the vertical dimensions of objects are lost entirely, foreshortened to negligible dimensions. A cow yard is more conspicuous than a church steeple, a sheep trough than a windmill; while hill features

are entirely lost to view unless the sun is so low as to produce specially conspicuous shadow effects. As a result, the most familiar landscape takes on an aspect of unreality, and one must re-learn it from the new point of view.

Another disturbing factor is the speed at which the plane travels. On the ground a motorist is accused of being a speed hog if he travels much over thirty-five miles an hour, and even at such a pace his passengers complain that they cannot take in the view. The speed of the aeroplane is rarely much under 100 miles an hour, so that before one can realise that he has passed a certain point he is twenty miles away. A new speed sense has therefore to be developed.

Certainly a thorough knowledge of the geological map of a district is one of the most useful guides to self orientation, since the outstanding geological features, so well known from the map *in two dimensions only*, spring forth from the unfamiliar setting as something tangible to which the mind can cling.

The writer's experience is that it takes something like one hundred hours of flying before one can sufficiently dissociate himself from the act of flying to concentrate all his faculties on systematic scientific observation. By this time also the unfamiliarity of the panorama has been overcome, and a new standard of topographic expression has been evolved. Even then, however, the speed of movement continues to be a disadvantage, and there is no time to make more than cursory notes during straight flight. Circling overcomes this to some extent, but the necessity for "banking" on turns puts the whole world on a slant which interferes considerably with one's appreciation of orientation of objects.

There is considerable diversity of opinion as to the limits of possibility of recognition of individual rock types from the air. Always with the proviso that *any* rock naming is tentative only, and liable to extensive modification as a result of petrological examination of actual specimens in the field and laboratory, I consider that it is legitimate to apply general names, provisionally, to the formations passed over. Where, as is always desirable, flight has been preceded by a ground reconnaissance of the area, it should be possible to make major differentiations with some confidence. Even in unknown areas one's general knowledge should make possible some generalisations, since, as a result of extensive experience, a "stock-in-trade" of

geological knowledge is gradually built up. Even in a country like Australia, where geological mapping is so incomplete, our general knowledge of the distribution of formations is now sufficient to provide indications as to probabilities, and we need expect no "geological surprises" of a revolutionary character.

It is, however, chiefly in relation to the mutual relations between the formations, in other words the fabric and structure of the district, that the aerial view shows its outstanding superiority. It is sometimes stated that there is nothing which can be seen from the air that cannot be seen on the ground. Strictly speaking this may be a fact, but practically it is not. There are many effects in an air view which depend on such properties as variations in reflecting power of soils of exactly similar colours, or on the habit or density of plant covering, which are entirely inappreciable when the light entering the eye of an observer on the ground strikes the objects at grazing instead of vertical incidence. The phenomena mentioned by no means exhaust the possibilities in this direction.

An example comes to the writer's mind in this connection. After months of devoted work in a locality in Queensland, a party of competent geologists had made no headway at all with detailed mapping. Criterion after criterion had been tried with no success, and admission of total failure appeared to be inevitable. In a preliminary flight over the area symmetrical soil pattern of a most conspicuous type was observed, which could not be other than a reflection of sub-surface geological structure in deeply decomposed sedimentary rocks. The ground party, including the writer, confidently returned to the spot in expectation of being able to trace such conspicuous colour differences on the ground—but were entirely unsuccessful. It was only later, after meticulous location of details from photographs, that it was ultimately found that the *sole visible difference in the soil was a slight variation in texture*, which could be noted only where sheep had passed over. On those bands which appeared dark from the air the sheep kicked up the soil appreciably, while on the "lighter" bands the sheep tracks were not so conspicuous. Colour variation, at grazing incidence of light, was not apparent.

It is a well known fact that after centuries of agriculture and archaeological research around some of the ancient temple sites in England, details of entirely unsuspected

engineering works of major importance have been recognised as soon as aerial observation has been brought into use.

Thus visual observation from the air would, even without other advantages, be a great boon to the geologist of the present and future in comparison with the facilities enjoyed by W. B. Clarke and his contemporaries. The greatest drawback, at present, is the high speed of travel. The day is rapidly approaching when the hovering aircraft will eliminate this difficulty, but such aircraft, though in use even now, have not, as yet, attained such perfection of development as to be universally desirable.

It is at this point that photography comes to our aid and instantaneously and permanently makes a record which is available for leisurely application and analysis afterwards, reducing the high cost of air travel to negligible proportions in relation to the advantages gained, and providing, in a few minutes, material for researches which may extend over years.

Even single and isolated photographs taken from heights well above the surface would supplement to an important extent the geologist's notes. Still more valuable are systematic serial photographs so arranged as to give a composite picture of an area far too large to be included within the range of a single exposure.

Single exposures are of several different kinds, each possessing distinctive advantages and limitations.

The simplest type are what are termed "high obliques", that is pictures taken from an aeroplane with the camera pointing out towards the horizon, and therefore at a comparatively small angle of depression. The term "high" in this case does not refer to the altitude of the aeroplane above the ground, but to the "high" angle of departure of the axis of the lens from the vertical.

Such pictures have the advantage that each of them covers an enormous area of country. Unfortunately this is offset by the fact that, as the background is approached, the scale of the picture decreases so rapidly that even major features become invisible. Moreover, it rarely happens that the atmosphere is so clear that the "distance" is not almost completely obscured by haze or dust. In the foreground, however, the delineation of features may be ideally sharp.

The obvious disadvantage of variation of scale in different parts of the picture can be overcome, and the pictures can be made amenable to direct measurement

of direction and distance. The ordinary laws of perspective apply, but the preparation of the "graphical nets" required for direct measurement is extremely exacting, and different "nets" are required for every variation in height and tilt. Nevertheless such "high obliques" are very extensively used in some countries, notably in Canada, where there are vast stretches of lake and forest country of low relief, almost impassable to the ordinary traveller. The method becomes less useful in areas where there is any considerable topographic relief. In the first place it is obvious that high points will tend to obscure large areas behind them and, in the second place, direct measurement becomes practically impossible.

"High oblique" photographs from low and moderate altitudes have a special value in some instances. They do *not* lend themselves readily to measurement but, for the reason that they depict the landscape from a more or less familiar angle, they give a better representation of features than do the less ordinary looking pictures taken under other conditions. The writer made the mistake of not realising this during the whole of his earlier work, but the value of pictures of this kind was brought home to him through a few casual exposures made with a hand camera. Many of the pictures taken during the 1927 flying boat expedition to Papua come within this category.

"Low obliques" are photographs taken with the axis of the lens more or less perpendicular to the ground surface. They therefore approximate to "verticals", which are the principal aim of most aerial photographic survey. Rarely, indeed, is a "low oblique" exposure intentionally made in the course of such a survey, but since such pictures can be taken with simple apparatus and without the elaborate precautions which are necessary to obtain a close approximation to verticality, consideration of them cannot be neglected entirely, and they may be used extensively in reconnaissance work.

Not possessing a "horizon line", as do "high obliques", they are not directly amenable to the rules of perspective drawing; while, not being vertical, they do not represent even an approximately correct orthographic projection of a section of the earth's surface. Owing to the marked tilt they are subject to a very considerable amount of distortion. Provided, however, there is an adequate amount of "ground control", it is possible, by mathematical analysis, to carry out a process of "rectification" which

produces a rectangular grid for each photograph, making it amenable to direct measurement of directions and distance.

If the departure from verticality is not too marked, and if there is sufficient ground control available, the simplest method of effecting rectification is by re-photography. The positive print, on glass or paper, is held in a suitable frame provided with movements of tilt in two rectangular directions, and of linear movement in three directions. The focusing frame of the camera, and with it the sensitive plate, has similar movements, and the lens panel is also capable of free movement. By suitable adjustment, which can be calculated in advance, it is possible to obtain from the tilted positive a copy which is a true vertical representation. At the same time the linear scale of the picture can be adjusted to any desired extent, so that the method is exceedingly elastic in its application.

As noted above, the very great majority of photographs taken in connection with organised aerial survey operations aim at being "verticals". The cameras employed are marvels of accuracy and ingenuity and, mechanically and photographically, are as perfect as it is possible to make them. It is not surprising, in such circumstances, to find a standard type of aerial survey camera weighing well over half a hundredweight, and costing from £500 to £700.

Even when every precaution is taken, however, it is not always possible to ensure that the axis of the lens is at right angles to the plate within the finest limits of accuracy, and still less to ensure that that axis is strictly vertical at the moment of exposure. It follows, then, that almost all supposedly "vertical" photographs are really to be regarded as special cases of "low obliques" and treated accordingly. In most instances, where required only for geological work, rigid rectification is not called for, since the slight uncertainties as to the exact positions of junction lines between adjacent formations, particularly in soil-covered and plant-covered areas, render unnecessary the application of meticulously accurate measurement. What is usually necessary is the location of boundaries within a few inches, or even feet, and this can be carried out even with unrectified prints, particularly when it is borne in mind that the aerial observations, including photography, are a means to an end, not the end in themselves, and that

actual measurement on the ground must follow the application of aerial survey.

Not the least valuable property of aerial photographs is that an observer on the ground can use them to locate himself in relation to the topography. This is an enormous advantage when working in deep gullies.

In the above discussion the necessity for "ground control" has been stressed repeatedly. The nature and amount of such control varies with the object of the survey. For certain purposes, where the highest grade of accuracy is necessary, costly refinements are called for, and specially constructed beacons may have to be used for the purpose. For the great majority of purposes, however, accuracy *within the limits of representation on paper at the scale of the map used* must be regarded as necessary and sufficient. Certainly highly refined theodolite measurements are amenable to mathematical computation of the most rigorous type, and such measurements are called for in geodetic operations. The results of the computations, however, are far beyond the ability of the draughtsman to transfer to paper and, if graphical representation and not mathematical computation is the aim of the survey, such high accuracy is fictitious and wasteful.

For any purpose requiring, at most, fine draughtsmanship for presentation of results, adequate ground control can usually be obtained by making use of existing objects which can be recognised in the resulting pictures with sufficient sharpness of detail. In general six ground control points per print are required, and these must be suitably distributed over the area covered by the picture. Four such points are necessary for rectification, but the other two are desirable for combining individual prints into a composite picture.

While in general it is advisable to have the ground control points selected and trigonometrically fixed in advance, this is not absolutely essential and, in some circumstances, it may be preferable to select suitable points from the finished prints and then to fix their positions by survey.

For the purpose of carrying out the calculations required in this process of rectification elaborate mathematical analysis has been made and methods and formulæ have been developed. In this paper it is not necessary to deal with this aspect in any detail. Reference may be made to an exhaustive treatise on the subject, namely M. Hotine



"Surveying from Air Photographs", London, Constable and Co. Ltd., 1931, and to various War Office papers forming "Professional Papers of the Air Survey Committee", largely from the same pen.

While much valuable information can be obtained from individual photographs of the types mentioned above, the great bulk of the aerial survey work which is being carried out so widely at the present time utilises composite photographs obtained by the combination of large numbers of prints, so arranged as to provide considerable overlap between contiguous prints, and thus cover a large area. Such composite pictures are referred to as "strips", when only a single linear series is employed, and "mosaics" when two or more "strips" are combined, side by side, to cover still larger areas.

It is chiefly for the production of such strips that the aerial camera has been elaborated. When properly set up, the instrument makes exposures at predetermined intervals of time so as to secure the desired overlap between adjacent exposures, winds off the film, and prepares a new section for exposure, sets the shutter, indicates to pilot and photographer the preparedness for each operation, exposes a signal to the personnel at the moment of exposure, and photographically records such essential details as height, compass bearing, serial number of the exposure, trim of the plane at the moment of exposure and written notes relating to lens and filter equipment, locality and so on.

With such a list of operations performed mechanically one would be pardoned for assuming that there is little left for the "human element" in the process; but this is very far from being the case. The ultimate value of the operations depends almost entirely on the training and skill of the operators at various stages in the process.

Even a very skilful pilot cannot immediately fly so straight and so level as to permit the camera to do its part perfectly. What passes for straight and level flying in ordinary commercial aerial operations is quite inadequate for the special purposes of aerial photographic survey. When the writer was investigating this subject in America some years ago he was informed by one of the leading commercial firms engaged in aerial survey that it gave its pilots a full year of training flying before entrusting them with actual survey operations.

Since the flying has to be done at very high altitudes—very rarely at less than 10,000 feet, and frequently in the

neighbourhood of 15,000 feet—flight by reference to landmarks is ruled out of the question, and steering by compass is required. The pilot must be thoroughly trained, therefore, in the behaviour of the compass in relation to tilt in various directions. In any circumstances the air is so unstable an element that its internal movements tend to introduce almost inappreciable variations, recognition of which calls for long experience.

The "trim" of the aeroplane, both fore and aft and laterally, is recorded at the instant of exposure by photography on the margin of the sensitive film of two suitably oriented spirit levels or some form of pendulum. These are competent to provide accurate information only if the foundation upon which they stand is not itself changing its tilt at the moment. If, however, the plane is either pitching or rolling appreciably at the time, the bubbles of the levels are affected by centrifugal force and fail to give a reliable indication of the trim. Hence the great importance of the pilot seeing that no sudden movement other than forward movement in the line of flight is occurring at the moment of exposure. This risk is minimised by the fact that the camera automatically lights a signal lamp in the pilot's cockpit, usually five seconds before exposure, giving him time to check any violent movement. It is preferable that there should be a *steady* tilt at that moment, rather than that the aeroplane should be in the act of becoming level.

It is largely this failure of the spirit levels (or their equivalent) to record the exact conditions at the moment of exposure that necessitates the employment of so much ground control in accurate work.

Even when all possible care and skill have been employed in the flight, it is impossible entirely to eliminate unpremeditated movements due to "bumps" and air pockets. It is therefore inevitable that a certain amount of rectification must be employed.

In order that a uniform linear scale may be maintained throughout the mosaic it is obviously necessary that the altitude of the aeroplane above the surface should be kept within very narrow limits. For this purpose the aneroid barometer is employed. Anyone who has worked with such an instrument is only too well aware of its sensitiveness to external and internal sources of error, and appreciates that, under the special conditions of use in aircraft, the results must be regarded as approximations only.

The mobility of the medium introduces still other complications which call for attention and correction. Obviously the time interval between successive exposures necessary to secure a prearranged amount of overlap must be adjusted to suit the "*ground speed*" of the aircraft. This is compounded of the *air speed* in the direction of flight and the *direction and velocity of the wind*.

Considering only the component of the wind's velocity in the direction of the flight, this is additive for a tail wind and subtractive for a head wind; so that the effects must be measured and allowed for by both pilot and photographer, and these effects are widely different in a go-and-return flight. In photography of parallel strips it is often preferable to return to the starting point, so that all exposures are made when flying in the same direction. In the case of long strips, however, particularly when the angle of incidence of the sun is low, such delay may introduce undesirable variations in shadow effects which interfere seriously with the results in the composite picture. If exposures are made in both directions the time interval has to be recalculated, and the camera mechanism reset, involving risk of error.

The lateral component of the wind velocity produces "drift" in the flight; the resultant direction of motion of the plane and the velocity in that direction, being the resultant, on the parallelogram law, of the forward velocity of the plane, and the direction and velocity of the wind.

The lateral drift produced in this way is neutralised by the pilot by setting the nose of the aeroplane sufficiently to windward to "make" a direct course. This is part of the elementary navigation of the plane. If the camera were set in the machine with the sides of the photographic plate respectively parallel to and perpendicular to the long axis of the plane, it is obvious that successive pictures in a strip would be "offset" laterally. This is spoken of as "crab". (See Fig. 1.)

This effect is neutralised by mounting the camera on a platform which is capable of rotation in the horizontal plane. The fore and aft edge of the plate can thus be turned so that it is parallel to the "course made", and not to the axis of the aeroplane ("course set").

With all precautions, however, there are residual and inherent defects and distortions which necessitate more or less drastic correction, and which prevent *absolute* substitution of photographic measurement for direct

measurement. The effect of tilt, even slight tilt, has been dealt with above.

More basic in character, and more difficult to detect and eliminate is the distortion due to terrain features. Obviously only objects on one and the same horizontal plane can be represented to scale even by the most perfect of cameras,

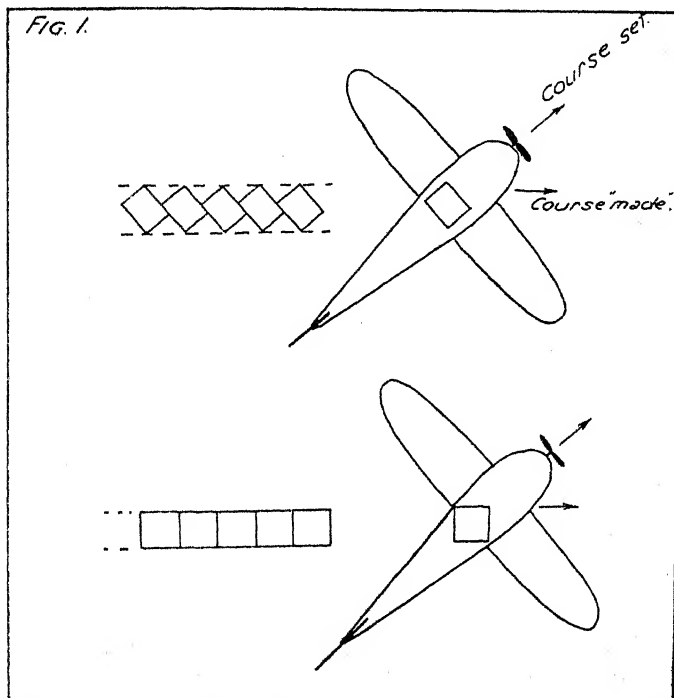


Fig. 1.—Effect of "Crab" due to lateral drift in flight, and its elimination by rotation of camera.

perfectly levelled and adjusted. Objects nearer to or further from the camera than those on the plane of reference will be reproduced on larger and smaller scales respectively. This type of distortion can be eliminated only by piecemeal rectification, and then only to a partial extent.

At the principal point of the photograph all rays are perpendicular to the plane of the plate, and therefore positions of objects are correctly represented. Towards the borders of the plate, however, the rays are oblique to the

planes of object and its plate image. When once a plane of reference has been assumed for the section of landscape under representation, any object lying above that plane in the peripheral regions of the plate will be represented

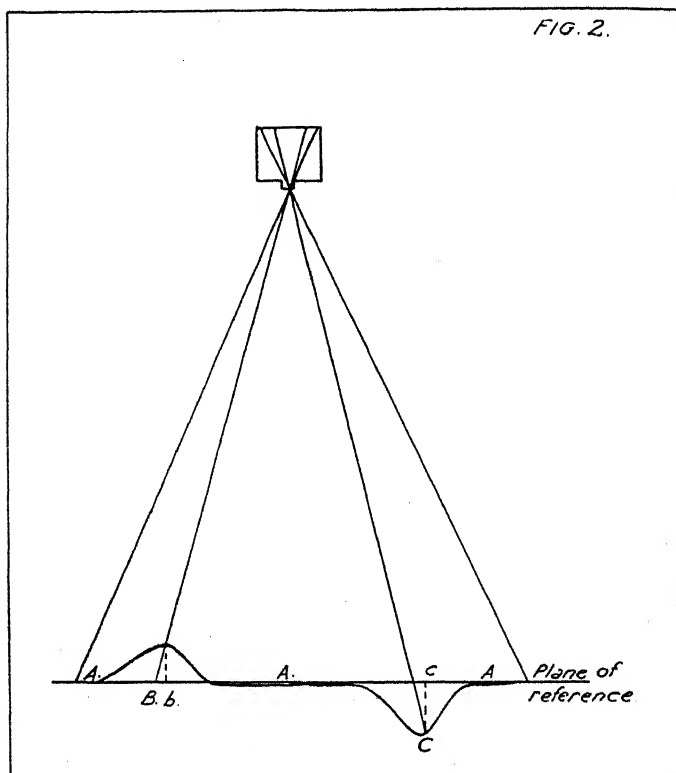


Fig. 2.—Distortion due to irregularities in altitude of terrain. Objects, A, A, A, lying in the plane of reference are truly represented in scale and position. Objects above that plane, like B, are displaced from the centre in reference to their orthographic projections, *b*, on the plane of reference. Objects below the plane of reference are displaced centrewards, *C : c*.

too far from the centre, while objects below the plane of reference will be too close to the centre. (Fig. II.) Except in the most rigid analysis this type of distortion can be assumed to be strictly radial from the principal point of the plate.

The wider the angular aperture of the lens, the greater will be the peripheral distortion. An additional disadvantage of very wide angle lenses is that optical perfection is very difficult to obtain, and the covering capacity of the lens deteriorates. The widest angle ordinarily used in British aerial cameras is about  $70^{\circ}$ . With such a lens there is a decided falling off in sharpness towards the edges of the pictures, with diaphragm apertures large enough to give adequate exposure, and the corners of the plate are barely covered.

This limitation in angular aperture, in conjunction with economic considerations of height and flight, imposes definite lower limits on the linear scale of aerial photographs.

These distortions are of great theoretical and practical moment when it becomes necessary to build up individual prints into composite pictures forming either "strips" or "mosaics". The hit or miss method of "matching details" soon leads to cumulative errors of serious dimensions, especially since the details which have to be matched are necessarily peripheral in position. If such details are out of the plane of reference their displacements are in opposite directions in adjacent prints.

Methods have been evolved whereby errors of this character can be reduced to small dimensions, and the resulting compilation can be made a close approximation to accuracy. A full discussion of the methods is given by Hotine (*loc. cit.*).

Marginal error of this kind is reduced considerably if the photography is carried out in such a way as to eliminate the necessity for using the extreme margins of the pictures, in other words, if the overlap of successive prints is made sufficiently large. For another reason, also, it is essential that liberal longitudinal overlap should be assured. With every possible precaution it happens occasionally that some slight mechanical hitch, or a sudden "bump" at the moment of exposure, may damage or blur one exposure, or that accidents in the dark-room may lead to the same result. It is therefore essential that every object in the landscape should be included in *three* successive pictures, and therefore longitudinal overlap in each "strip" should exceed 50 per cent. Excessive overlap rapidly increases the expense of the work, so that the commensurate advantages are purchased at too high a price. Commonly a longitudinal overlap of sixty per cent. provides all the advantages which can reasonably be expected.

When an area wider than can be covered by a single "strip" has to be photographed, the construction of a "mosaic" becomes necessary. Parallel strips have to be flown and photographed, placing a greatly added responsibility on both photographer and pilot. In addition to the longitudinal overlap which is secured mechanically by proper adjustment of the camera mechanism, adequate lateral overlap is required also. Normally this need not be so extensive as longitudinal overlap, and usually 25 per cent. is sufficient.

Any failure of lateral overlap produces gaps in the finished mosaic which can be filled in only by reflight, which may be prohibitively costly, especially in areas far from the air and photographic bases. On the other hand, excessive overlap leads to much redundant photography, with consequent increase in the cost of the work.

If a high degree of skill has been shown in the various operations, the resulting mosaic should be a very close approximation to a true scale representation in azimuth and dimensions of the features of the area photographed. In other words it is a "map". Any ordinary map, made by conventional methods, is merely a compilation of observations made by an individual, and represents his *reasoned selection* of data to be included. No such map can possibly be complete. The amount of detail which can be noted and included is a function of the time taken, both in field and drawing office, and the cost of the work varies with the time.

An aerial photographic map, on the other hand, shows every detail capable of being recorded photographically. The cost is not affected by the amount of detail shown. Further, there being no discriminatory selection, all *kinds* of detail receive equal treatment. For this reason one mosaic may be useful for a great variety of purposes. Thus engineers may use it for such diverse purposes as road and railway location, water conservation, irrigation, power line location, town planning and so on. Foresters may find most of the information required by them recorded; geologists have a detailed record of outcrops and structures; and a great variety of other uses may be subserved. The rather high initial cost of the work, possibly prohibitive for any individual purpose, may therefore be shared between a considerable number of interests, with mutual advantages to all. Some years

ago a complete map of this kind was made of the districts surrounding Los Angeles, the costs being pooled between city authorities, railway companies, irrigation and water supply schemes, oil companies and others, the individual expenses being almost negligible.

So far we have been considering the advantages of two-dimensional representation only. Great as are such advantages, they are probably inferior to those gained by the introduction of a third dimensional sense through stereoscopic vision.

The estimate of relative distances of objects from the eye of an observer is gained in two different ways. By life-long training of hereditary instinct, using an instantaneous estimate of relative sizes of objects, we are able to determine distances. This method needs the use of only one eye, and is effective where familiar objects are involved, but may lead to curious illusions when unfamiliar objects are introduced. A leading British physiologist who had lost an eye records that, on one occasion in his own drawing-room, he distinctly saw a rose growing out of the top of the bald head of a distinguished visitor. This power of estimating relative distances is often popularly confused with true stereoscopic vision.

Stereoscopic vision proper is exclusively binocular, and depends on the physiological fusion of two independent and slightly different images seen from slightly different points of view, separated in the ordinary case by the interocular distance of the observer. The effect is one of parallax, and is simply tested by holding the head perfectly rigid and viewing distant objects, past a fixed foreground, by the two eyes separately. There is a *relative* displacement between foreground and background objects as seen by right eye and left eye respectively.

The two pictures of an ordinary stereoscopic photograph differ in the same way as do the images seen by the two eyes, and are actually taken by a double camera for this purpose. The inspection of two *identical* pictures through a stereoscope produces an *illusion* of "depth" owing to auto suggestion combined with instinctive size estimation as explained above. One has only to compare a pair of identical prints with a true stereoscopic pair, however, to be convinced of the essential difference.

True stereoscopic vision is confined to persons with two eyes both functioning normally and approximately



equally. The writer is unfortunately competent to make this assertion from personal experience.

Adjacent overlapping pictures of an aerial photographic survey are related to one another exactly in the sense of a stereoscopic pair, though the effect is exaggerated as compared with that obtained in ordinary human vision. The effective difference in point of view amounts to hundreds of yards instead of some two and a half inches. When the pictures are "combined" in a suitable stereoscope, enabling normal eyes to obtain the *effect* of simultaneous vision, an enormously exaggerated perspective effect is obtained. The ordinary observer sees the land surface as it would appear to a giant whose interocular distance was the same as the interval between exposures.

Examination of such exaggerated stereoscopic pairs through even a simple stereoscope is of enormous value in giving a qualitative impression of differences in height of the objects represented. There is no doubt also as to improvement in the *sense* of clarity of representation, though this impression is psychological only. Even such qualitative stereoscopic effect is exceedingly valuable in the appreciation of geological structure as revealed by aerial photography, and numerous types of stereoscope have been introduced for examining air photographs.

This, however, is only the beginning of the value of stereoscopic examination.

If in the field of view of the stereoscope there are introduced two artificial signals or marks, at the same distance from the principal points of the prisms or lenses of the instruments, and capable of being moved closer to one another or further apart, these signals are "combined" by the eyes of the observer into one image, which takes its appropriate place in regard to the "depth" of the picture. The marks appear to "float" in the field of view. By causing the signals to approach one another, the "floating mark" is brought closer to the observer. By separating them the "floating mark" sinks back towards the background. By suitable adjustment the mark can be made to stand at any desired "depth" in the picture, and can be used as a definite point of comparison. By relative movement between the pictures and the signals relative heights of objects can be estimated with great precision, and the purely qualitative impression gained from an ordinary stereoscopic pair can be rendered quantitative.

This is not the place to enter exhaustively into the theory and practice of stereoscopic vision or of the instruments which have been introduced to convert the observations into precision measurements. Reference may be made to the technical works on the subject cited above.

By various devices, more or less rigidly correct in their mathematical foundation, different designers have produced stereo-comparators, stereo-planigraphs and stereo-cartographs which *mechanically* record the successive positions of the "floating marks" in relation to the topographic pictures and which facilitate the production of contoured maps.

There is some little difference of opinion amongst cartographers in relation to the admissibility of the results so obtained. Comparison between contoured maps made by such organisations as the United States Geological Survey and those of the same areas prepared from aerial photographic surveys, strongly suggests to the mind of a layman in the practice of accurate surveys that there are advantages in the photographic method. It appears obvious that essential considerations of time available in the field have necessitated a certain amount of "smoothing out" in the plane tabling, while it is possible, in the stereoscopic plotting instruments, to make the "floating mark" follow absolutely every visible irregularity in the "solid" picture.

In many geological operations, particularly in seeking for domal structures in very slightly warped formations in oil prospecting, ordinary dip and strike measurements with compass and clinometer are ineffective. Minor and accidental irregularities in attitude, and minor uncertainties in regard to the exact point of a particular stratum under examination, introduce errors large in comparison with the quantities to be measured. In such instances the application of the "contour outcrop method" is the only approach to the problem which can be satisfactory. While, of course, this method can be, and is applied in ordinary field operations, the ease and elegance of application by means of aerial photography has to be experienced to be appreciated.

Enough has been said to indicate that, in this new method, there are inherent advantages which must be seriously considered in all geological survey operations in the future. The new methods cannot supplant the time-honoured ones of careful and exhaustive examination

on the ground. The *additional* advantages, however, are so marked as to justify the cost involved. Sooner or later it will come to be realised that, while no amount of aerial survey can replace ground observation, no geological survey can be considered complete and satisfactory until the area has been subjected to aerial photographic survey, followed by stereoscopic inspection and *measurement* of the resulting prints.

Let us, then, as geologists, become more and more air-minded. The cost will be considerable both in men and money, for the safety of air travel, though constantly increasing, is not yet absolute. Some broken necks must be included in the price we have to pay for our greatly increased efficiency, but the cost must be faced with equanimity. Let us keep, also, in the forefront of our minds two other important facts in relation to the new methods. Firstly, they supplement, and do not supplant, the methods of Clarke and his contemporaries; secondly, the new methods are not learnt in an hour; they require just as much study and mental and physical discipline as does the employment of any other branch of the science of geology, and we must be prepared to accept and develop the discipline. I hope to live long enough to see the study of interpretation of aerial photographs, based on personal observation from the air, introduced as an essential feature of advanced geological training in our teaching institutions. So will the geologists of the future amplify and extend the pioneer work of the great man whose life and work we commemorate tonight.

### EXPLANATION OF PLATES.

#### PLATE I.

Above.—Byro Plain, North-West Division, Western Australia. Soil produced in deeply weathered formations, devoid of normal outcrops, by nearly horizontal sediments (Permo-Carboniferous). Several faults can be recognised.

Below.—Poole Range, Kimberley Division, Western Australia. Cañon dissection in nearly horizontal sediments (Permo-Carboniferous). Variations in topography in the upper (Poole Range) beds and in the lower (Grant Range) beds can be seen.

#### PLATE II.

Above.—King Leopold Ranges, Kimberley Division, Western Australia. Unconformity between upper and lower Proterozoic formations.

Below.—Near Horseshoe Creek, Northern Territory. Overthrust basic dykes in granite. Note the control of stream development by faulting and jointing.

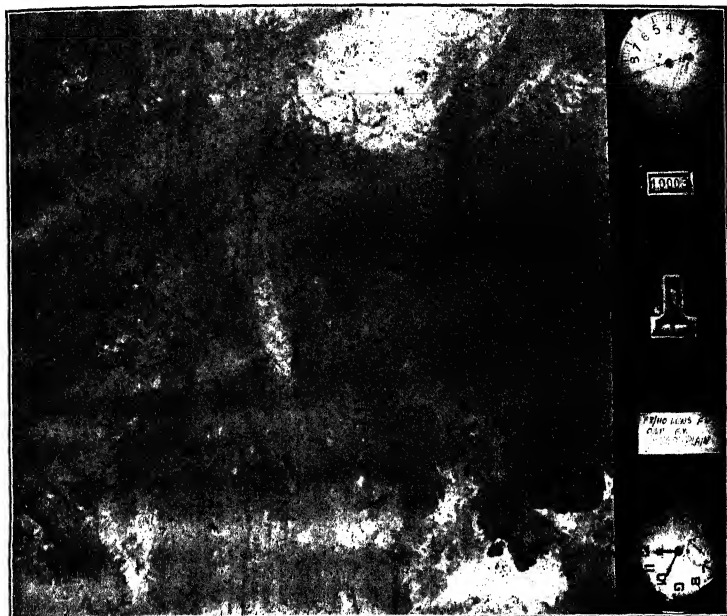
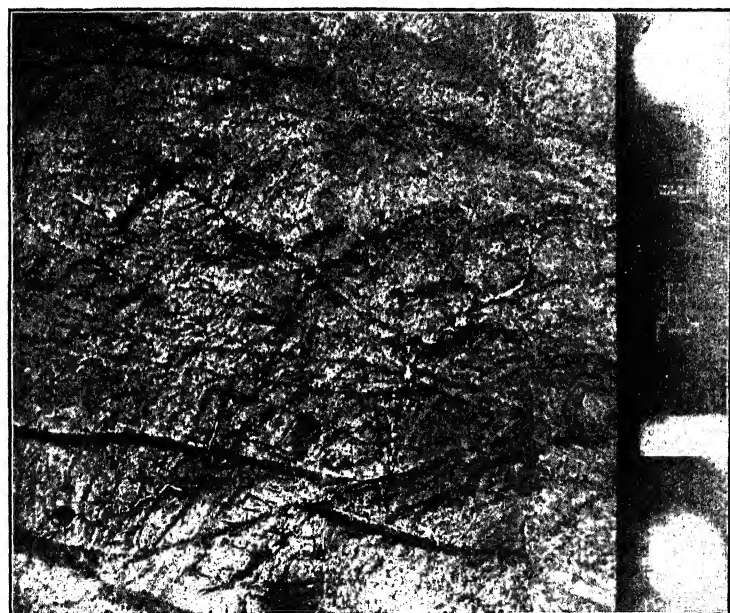
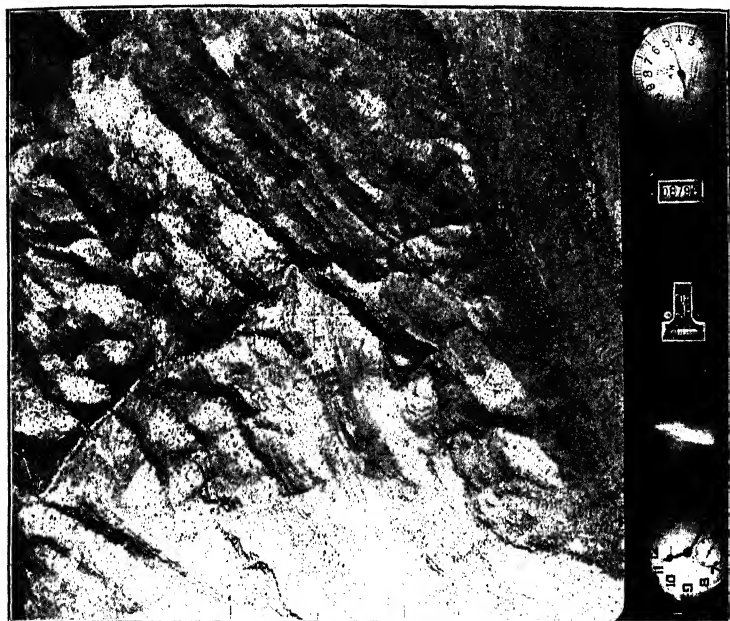


Figure 1. The effect of the concentration of the *Agrobacterium* suspension on the transformation efficiency of *Agrobacterium* strains.

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COMPOUNDS FORMED BY MERCURY SALTS WITH  
TERTIARY ARSINES.

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(Manuscript received April 18, 1936. Read, June 3, 1936.)

Various compounds of mercury salts with basic substances are described in the literature. With ammonia the following have been isolated:  $\text{HgCl}_2 \cdot \text{NH}_3$  (Naumann, *Ber.*, 1899, 52, 1000),  $\text{HgCl}_2 \cdot 2\text{NH}_3$  (Andre, *C.R.*, 1899, 108, 233, 290),  $2\text{HgCl}_2 \cdot 3\text{NH}_3$  (Varet, *C.R.*, 1899, 109, 941),  $3\text{HgCl}_2 \cdot 2\text{NH}_3$  (Holmes, *J.C.S.*, 1918, 113, 74), and  $\text{HgCl}_2 \cdot 12\text{NH}_3$  (Franklin & Kraus, *Am. Ch. J.*, 1900, 23, 300). Compounds with hydrazine are of the type  $\text{HgCl}_2 \cdot \text{N}_2\text{H}_4$  (Hofmann & Marburg, *Ann.*, 1899, 305, 191) and with hydroxylamine  $\text{HgCl}_2 \cdot 2\text{NH}_2\text{OH}$  (Adams, *J.A.C.S.*, 1902, 28, 198). Compounds with other bases such as pyridine, quinoline and aniline are of two types,  $\text{HgCl}_2 \cdot \text{B}$  and  $\text{HgCl}_2 \cdot \text{B}_2$ , where B represents one molecule of the base (Staronka, *Bull. Acad. Sci., Cracow*, 1910, 372; Schralder, *Zeit. Anorg. Chem.*, 1905, 44, 14).

In the present communication we record results obtained in studying the behaviour of mercury salts towards tertiary arsines, which behave in this respect in much the same way as ordinary nitrogen bases. The arsines chosen for this investigation were phenyl dimethyl arsine and diphenyl methyl arsine, because of their ease of preparation in a pure state, and also because of the fact that they have been found to combine readily with salts of platinum, silver, and copper (Burrows & Parker, *J.A.C.S.*, 1933, 55, 4133; *Proc. Roy. Soc. N.S.W.*, 1934, 68, 39; Burrows & Sanford, *Proc. Roy. Soc. N.S.W.*, 1935, 69, 182).

It was observed that, when an alcoholic solution of diphenyl methyl arsine was added to a boiling concentrated solution of mercuric chloride in alcohol (in equimolecular proportions) a white insoluble compound was precipitated. This precipitate could be recrystallised from a large volume



of hot alcohol in the form of colourless needles melting at  $186^{\circ}\text{C}$ . On analysis the compound was found to contain one molecule of mercuric chloride, co-ordinated with one of arsine, i.e.  $[\text{Ph}_2\text{MeAs.Hg}]\text{Cl}_2$ . Similar compounds were obtained with mercuric bromide and mercuric iodide, the former being white and the latter yellow. Working with boiling solutions as above, the proportion of arsine to mercury salt was varied over a wide range, but in every case the same type of compound was obtained. It appeared at this stage that the only type of compound formed was one in which one molecule of mercury halide was co-ordinated with one of arsine.

The behaviour of mercurous halides towards diphenyl methyl arsine was next examined. For this purpose the arsine (1 mol.) was dissolved in hot alcohol, and added to mercurous chloride (1 mol.), suspended in a relatively small volume of the same solvent at the boiling point. The suspension became black owing to the separation of mercury. On immediate filtration and cooling, colourless glistening plates were obtained, melting at  $130^{\circ}\text{C}$ . Examination of this compound proved that the mercury was present in the mercuric state, indicating that in the reaction the mercurous chloride had broken down into mercuric chloride and mercury. The conditions were then varied, and mercurous chloride was treated with excess of diphenyl methyl arsine in warm alcohol and the product washed with warm alcohol. On analysis the colourless crystals were found to have the formula  $\text{HgCl}_2 \cdot 2\text{Ph}_2\text{MeAs}$ . This experiment pointed to the fact that at the boiling point one molecule of arsine was eliminated. These results indicated that two series of compounds could be formed from the arsine with either mercurous or mercuric salts; at low temperatures  $\text{HgCl}_2 \cdot \text{R}_2$ , where R represents one molecule of the arsine, and on boiling,  $\text{HgCl}_2 \cdot \text{R}$ . Experiments were carried out at a temperature of  $-5^{\circ}\text{C}$ . with various relative amounts of arsine, but no other compound could be isolated. By repeating the original experiments with one molecule of mercuric chloride and two of diphenyl methyl arsine and keeping the temperature below  $50^{\circ}\text{C}$ . the compound  $\text{HgCl}_2 \cdot \text{R}_2$  was readily obtained in a pure state.

Compounds were obtained with other mercury halides and also with phenyl dimethyl arsine. It is interesting to note that bis phenyl dimethyl arsine mercuric chloride could not be obtained in the solid state.

## EXPERIMENTAL.

*Diphenyl methyl arsine mercuric chloride*  $[\text{Ph}_2\text{MeAsHg}]\text{Cl}_2$ : To a solution of mercuric chloride (1 mol.) dissolved in the minimum volume of boiling alcohol (98%), a hot alcoholic solution of diphenyl methyl arsine was slowly added with stirring. A white amorphous precipitate separated, which was recrystallised from a large volume of boiling alcohol in colourless needles melting at  $186^\circ \text{C}$ . The compound is only sparingly soluble in cold alcohol or acetone and insoluble in water, chloroform, benzene, ether or ethyl acetate. On boiling in water it is decomposed, with liberation of the arsine.

Found:  $\text{Hg}=38.4$ ,  $\text{As}=14.0$ ,  $\text{Cl}=13.7$  per cent.

$\text{C}_{13}\text{H}_{13}\text{AsHgCl}_2$  requires  $\text{Hg}=38.9$ ,  $\text{As}=14.5$ ,  $\text{Cl}=13.75$  per cent.

*Diphenyl methyl arsine mercuric bromide*  $[\text{Ph}_2\text{MeAsHg}]\text{Br}_2$  was prepared in a similar manner to the above, using mercuric bromide. It crystallises in colourless needles melting at  $142^\circ \text{C}$ ., and resembles the chloride in solubilities.

Found:  $\text{Hg}=33.1$ ,  $\text{As}=11.8$ ,  $\text{Br}=26.1$  per cent.

$\text{C}_{13}\text{H}_{13}\text{AsHgBr}_2$  requires  $\text{Hg}=33.2$ ,  $\text{As}=12.4$ ,  $\text{Br}=26.4$  per cent.

*Diphenyl methyl arsine mercuric iodide*  $[\text{Ph}_2\text{MeAsHg}]\text{I}_2$  was obtained from mercuric iodide and the arsine in boiling alcohol by cooling and scratching. The solution at first became yellow and then deposited a finely crystalline cream-coloured precipitate. Without scratching the compound separated as an oil which subsequently solidified. On recrystallisation from alcohol it was found to melt at  $116^\circ \text{C}$ . It resembles the chloride in solubilities. It is interesting to note that the chloride has the highest melting point and the iodide the lowest.

Found:  $\text{Hg}=28.4$ ,  $\text{As}=10.2$ ,  $\text{I}=36.2$  per cent.

$\text{C}_{13}\text{H}_{13}\text{AsHgI}_2$  requires  $\text{Hg}=28.7$ ,  $\text{As}=10.7$ ,  $\text{I}=36.3$  per cent.

*Bis-diphenyl methyl arsine mercuric chloride*  $[(\text{Ph}_2\text{MeAs})_2\text{Hg}]\text{Cl}_2$ : Mercuric chloride (1 mol.) was suspended in a small volume of alcohol (98%) at  $50^\circ \text{C}$ ., and a warm alcoholic solution of diphenyl methyl arsine (2 mols.) slowly added. At first a white precipitate formed, but this gradually dissolved as the arsine was added. The clear solution on scratching deposited glistening pearly plates melting at  $131^\circ \text{C}$ . The compound is insoluble in all the ordinary solvents at room temperature, and on heating with liquids such as alcohol, ether, or benzene, it

decomposes with the separation of one molecule of the arsine.

Found:  $\text{Hg}=26.1$ ,  $\text{As}=18.9$ ,  $\text{Cl}=9.1$  per cent.

$\text{C}_{26}\text{H}_{26}\text{As}_2\text{HgCl}_2$  requires  $\text{Hg}=26.1$ ,  $\text{As}=19.7$ ,  $\text{Cl}=9.2$  per cent.

*Bis-diphenyl methyl arsine mercuric bromide*  $[(\text{Ph}_2\text{MeAs})_2\text{Hg}]\text{Br}_2$ , prepared in a similar manner to the corresponding chloride was obtained in fine white crystals melting at  $100.5^\circ \text{C}$ . Towards solvents it behaves in the same way as the chloride.

Found:  $\text{Hg}=23.0$ ,  $\text{As}=18.3$ ,  $\text{Br}=18.5$  per cent.

$\text{C}_{26}\text{H}_{26}\text{As}_2\text{HgBr}_2$  requires  $\text{Hg}=23.6$ ,  $\text{As}=17.8$ ,  $\text{Br}=18.9$  per cent.

*Bis-diphenyl methyl arsine mercuric iodide*  $[(\text{Ph}_2\text{MeAs})_2\text{Hg}]\text{I}_2$ , prepared like the above separated as an oil which readily crystallised. It melts at  $83^\circ \text{C}$ . This compound is readily soluble in cold acetone, and is more stable towards hot solvents than the corresponding chloride and bromide. Nevertheless it is decomposed by boiling in these liquids.

Found:  $\text{Hg}=20.9$ ,  $\text{As}=15.2$ ,  $\text{I}=26.9$  per cent.

$\text{C}_{26}\text{H}_{26}\text{As}_2\text{HgI}_2$  requires  $\text{Hg}=21.3$ ,  $\text{As}=15.8$ ,  $\text{I}=26.9$  per cent.

The corresponding compounds with phenyl dimethyl arsine were obtained in a similar manner. They are all crystalline and colourless, with the exception of the iodides, which are yellow. Their solubilities are similar to those obtained with diphenyl methyl arsine. The melting points and analytical results are tabulated below.

*Phenyl dimethyl arsine mercuric chloride*  $[\text{PhMe}_2\text{AsHg}]\text{Cl}_2$ :  
M. Pt.,  $201^\circ \text{C}$ .

Found:  $\text{Hg}=43.7$ ,  $\text{As}=16.1$ ,  $\text{Cl}=15.6$  per cent.

$\text{C}_8\text{H}_{11}\text{AsHgCl}_2$  requires  $\text{Hg}=44.2$ ,  $\text{As}=16.5$ ,  $\text{Cl}=15.6$  per cent.

*Phenyl dimethyl arsine mercuric bromide*  $[\text{PhMe}_2\text{AsHg}]\text{Br}_2$ :  
M. Pt.,  $171^\circ \text{C}$ .

Found:  $\text{Hg}=36.5$ ,  $\text{As}=12.7$ ,  $\text{Br}=29.3$  per cent.

$\text{C}_8\text{H}_{11}\text{AsHgBr}_2$  requires  $\text{Hg}=37.0$ ,  $\text{As}=13.0$ ,  $\text{Br}=29.45$  per cent.

*Phenyl dimethyl arsine mercuric iodide*  $[\text{PhMe}_2\text{AsHg}]\text{I}_2$ :  
M. Pt.,  $144^\circ \text{C}$ .

Found:  $\text{Hg}=30.9$ ,  $\text{As}=10.8$ ,  $\text{I}=39.7$  per cent.

$\text{C}_8\text{H}_{11}\text{AsHgI}_2$  requires  $\text{Hg}=31.5$ ,  $\text{As}=11.1$ ,  $\text{I}=39.9$  per cent.

*Bis-phenyl dimethyl arsine mercuric chloride*  
 $[(\text{PhMe}_2\text{As})_2\text{Hg}]\text{Cl}_2$ : This compound could not be obtained in the solid state.

*Bis-phenyl dimethyl arsine mercuric bromide*  
 $[(\text{PhMe}_2\text{As})_2\text{Hg}]\text{Br}_2$ : M. Pt.,  $115^\circ \text{C}$ .

Found:  $\text{Hg}=27.2$ ,  $\text{As}=20.4$ ,  $\text{Br}=22.2$  per cent.

$\text{C}_{16}\text{H}_{22}\text{As}_2\text{HgBr}_2$  requires  $\text{Hg}=27.7$ ,  $\text{As}=20.7$ ,  $\text{Br}=22.1$  per cent.

*Bis-phenyl dimethyl arsine mercuric iodide*  
 $[(\text{PhMe}_2\text{As})_2\text{Hg}]\text{I}_2$ : M. Pt.,  $104^\circ \text{C}$ .

Found:  $\text{Hg}=24.4$ ,  $\text{As}=18.0$ ,  $\text{I}=31.2$  per cent.

$\text{C}_{16}\text{H}_{22}\text{As}_2\text{HgI}_2$  requires  $\text{Hg}=24.5$ ,  $\text{As}=18.3$ ,  $\text{I}=31.0$  per cent.

NOTE.—Considerable difficulty was encountered in the analyses of the above compounds. Ewin's method for the determination of arsenic in organic arsenicals was found to give inconsistent low results, due, probably, to the volatilisation of some of the arsenic. It was found more satisfactory to oxidise the arsenic to arsenic acid by means of chromic acid. For this purpose 0.15 to 0.2 gramme of the compound was placed in a conical beaker of 250 c.c. capacity and 5 c.c. of concentrated sulphuric acid were added. About 0.5 gramme of chromic acid was then added and the mixture heated on a sand bath to a moderate temperature. Care must be taken to avoid too high a temperature, which leads to the formation of anhydrous chromic sulphate, which is difficult to reconvert to the soluble hydrated form, thus interfering with the analysis. More chromic acid was added to the beaker as long as there was evidence of action, shown by the evolution of carbon dioxide. The beaker was then heated for a further ten minutes, the whole oxidation taking about half an hour. The beaker and contents were then cooled, diluted with water, and made slightly alkaline with a solution of sodium hydroxide and boiled. After removing the precipitated chromium hydroxide and mercuric oxide, the filtrate was made faintly acid with sulphuric acid, the arsenic reduced to arsenious acid by means of sulphur dioxide, and reoxidised in the ordinary way with a standard solution of iodine.

The halogen was determined by treating 0.2 gramme of the compound on the water bath with 10 c.c. of concentrated nitric acid in the presence of finely powdered silver nitrate. After diluting with water the insoluble

silver halide was filtered through a Gooch crucible or tared filter papers.

In the analysis of compounds containing iodine, the decomposition with concentrated nitric acid in the presence of silver nitrate yielded a white oily substance on the water bath, but on treatment with water this was converted to silver iodide. On cooling the oil, it was obtained in the solid form and found to have an indefinite melting point between  $75^{\circ}$  and  $90^{\circ}$  C. It contains both silver nitrate and iodide, and was identified as  $\text{AgI} \cdot \text{AgNO}_3$  described by Stürenberg (*Arch. Pharm.*, [2], 143, 12).

For the estimation of mercury two methods were followed. In the case of compounds containing chlorine or bromine 0.2 gramme was treated on the water bath with a slight excess of sodium hydroxide solution and the yellow mercuric oxide obtained as a fine precipitate, which was removed by filtration, washed with hot water and alcohol (to remove the last traces of arsine). The mercuric oxide was then dissolved in dilute hydrochloric acid, precipitated as sulphide, and weighed in the usual way. The method was found unsatisfactory in the case of compounds containing iodine. A modification of Seamon's volumetric method was found satisfactory for all compounds. Standard solutions of mercuric chloride and potassium iodide were prepared, and 20 c.c. of the former were titrated with the latter after the addition of concentrated nitric acid, using starch indicator. A blank titration was then made, using 2 c.c. of concentrated nitric acid diluted with water to the same volume as above, the volume of the potassium iodide solution found necessary being about 0.4 c.c. In the estimation 0.2 gramme of the compound was gently heated on the water bath with 5 c.c. of concentrated nitric acid till reaction was completed. The solution was diluted with 20 c.c. of water and the solution titrated with the potassium iodide solution as above.

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## THE BEN BULLEN PLUTONIC COMPLEX, N.S.W.

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(With two text-figures.)

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## 1. INTRODUCTION.

The writer has recently described the exogenous<sup>(10)</sup> and endogenous<sup>(11) (12)</sup> contact-zones of the Ben Bullen Plutonic Complex, and in connection with the endogenous contacts brief descriptions of the igneous rocks taking part in the reactions have already been given. These are repeated here, however, and it is shown that the rocks are members of the complex.

The intrusion has been mapped by the Geological Survey of N.S. Wales, and Fig. 1 is based almost entirely upon the original map by the survey officers.<sup>(3)</sup> Internal boundaries

and the subdivision of the mass into an earlier and later intrusion are due to the present writer.

## 2. FIELD RELATIONS.

The igneous complex covers an area of about 350 acres, and is a composite stock-like mass of irregular shape. The most prominent directions of jointing are N.-S., E.-W., N. 55° W., N. 70° W., and N. 40° E.

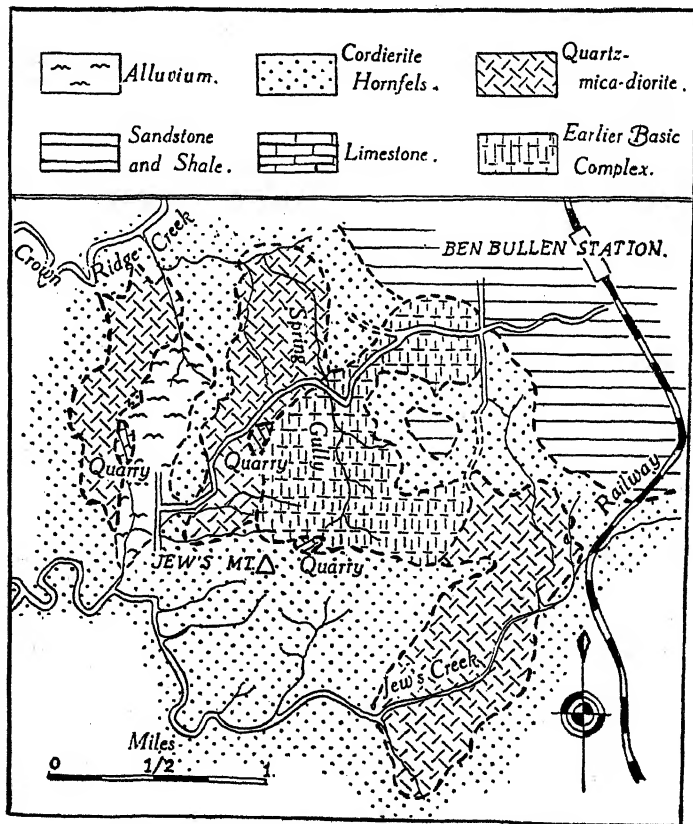


Fig. 1.—Geological Sketch Map of Ben Bullen.

The central portion is occupied by a basic mass which has been partly recrystallised and hybridised by a later intrusion of quartz-mica-diorite. The basic complex consists of a basified diorite enclosing numerous masses of

norite in varying stages of hybridisation, together with occasional patches of recrystallised gabbro which may also be hybridised.

Banded hornblende-gabbros occur at a few localities, but these are believed to be due to contamination with the limestone and will be described in a later publication.

Small fragments of the earlier complex have been collected amongst the limestone *débris* in the quarry on Por. 45, 46 and 47, Par. of Ben Bullen, and it is evident that these represent remnants of the first intrusion which invaded the limestone and together with the sedimentary rock formed the roof of the second magma chamber.

The later intrusion of quartz-mica-diorite partly surrounds the earlier complex, and immediately west of the main mass a chain of low, quartzite hills separates an apparently detached outcrop of quartz-mica-diorite. These hills evidently represent a portion of the roof of the intrusion, and the diorite is possibly continuous beneath this cover. Small patches of limestone, appearing to rest on the igneous rock, also point to the incomplete removal of the roof.

Occasional small dykes and veins of aplite and hornblende-lamprophyre occur as an end-phase of igneous activity.

### 3. PETROGRAPHY.

#### The Earlier Basic Complex and Related Hybrids.

Three main types make up the earlier complex, namely olivine-norite, norite or hypersthene-gabbro and recrystallised gabbro. It seems evident that the noritic complex was shattered and partly assimilated by a later intrusion of quartz-mica-diorite, and to avoid repetition the primary types will be described with the corresponding hybrids. The shattered norites are enclosed in a basified diorite, and, although this is a modified member of the later intrusion, it is so intimately related to the shattered norites that it is described with members of the earlier basic complex.

#### (i) *Olivine-norite and Hornblende-olivine-norite.*

The olivine-norite is believed to be the most basic member of the earlier complex, and one small mass, enclosed in the basified diorite, occurs about 40 chains S.W. of the N.E.



corner of Por. 1, Par. Ben Bullen. A small outcrop of the corresponding hybrid is met with in the middle of Por. 63.

In the hand specimen both are dense, dark, medium-grained rocks, and the hybrid type contains large (7 mm.), black "shimmer" plates of hornblende.

Under the microscope the normal type is panidiomorphic, granular, and sub-ophitic. The hybrid is highly poikilitic, and contains large irregular grains of hornblende, whilst the normal type shows only an incipient development of amphibole. The other minerals are plagioclase, augite, hypersthene, olivine, iron ores, and a little apatite.

Plagioclase occurs in laths with sutured boundaries, and these measure about 1 mm. The mineral is very clear and suggests an incipient recrystallisation, but no true crystalloblastic structures are developed. Mottling is suggestive of hybridisation.<sup>(8)</sup> The plagioclase is basic labradorite ( $\text{Ab}_{32}\text{An}_{68}$ ) with  $\alpha' = 1.563$ ,  $\gamma' = 1.573$ . It is optically positive, with a fairly large 2V. The extinction on sections  $\perp$  to 010 is  $38^\circ$ .

The pyroxenes occur in subidiomorphic prisms measuring about 2 mm. The augite is optically positive,  $Z \wedge C = 39^\circ$ , and polysynthetic twinning is common. The hypersthene shows relatively strong pleochroism. Both pyroxenes include olivine and iron ores, and in the hybrid type they are flecked with, and surrounded by, brown hornblende. In the normal type the pyroxenes show incipient amphibolization.

The olivine is optically negative, with a very large 2V;  $\alpha' = 1.680$ ,  $\gamma' = 1.720$ . According to Larsen and Berman<sup>(13)</sup> this indicates  $\text{Mg}/\text{Fe} = 78/22$ . Olivine occurs in rounded crystals which measure up to 1 mm. A good 010 cleavage is usually developed, and secondary magnetite often appears along cleavage planes and cracks. A little serpentine is sometimes present, but secondary amphibole is a more common alteration product. In the hybrid rock the olivine is included in brown hornblende.

Hornblende occurs in large (7 mm.) poikilitic plates in the hybrid type, and there is a slight development in the normal rock. In the latter narrow rims of pale green amphibole occur around all the minerals that are adjacent to plagioclase. This has already been figured.<sup>(9)</sup>

In the hybrid rock the brown hornblende appears to grow out into the plagioclase from cores of pyroxene, olivine and/or iron ores. The hornblende grows between the plagioclase laths and along the cleavages, and the

felspar thus appears to form normal idiomorphic inclusions. The mineral is optically negative;  $\alpha' = 1.662$ ,  $\gamma' = 1.690$ ; X=pale yellow, Y=reddish-brown, Z=reddish-brown ( $Z \gg Y > X$ );  $Z \wedge C = 24^\circ$ .

An analysis of the hybrid is given in column I below.

|                                   | I.     | II.    |
|-----------------------------------|--------|--------|
| SiO <sub>2</sub> ..               | 43.15  | 46.85  |
| Al <sub>2</sub> O <sub>3</sub> .. | 20.45  | 20.02  |
| Fe <sub>2</sub> O <sub>3</sub> .. | 3.79   | 2.30   |
| FeO ..                            | 7.98   | 4.60   |
| MgO ..                            | 7.82   | 10.16  |
| CaO ..                            | 14.03  | 13.84  |
| Na <sub>2</sub> O ..              | 0.71   | 1.32   |
| K <sub>2</sub> O ..               | 0.15   | tr.    |
| H <sub>2</sub> O + ..             | 0.58   | } 0.88 |
| H <sub>2</sub> O - ..             | 0.15   |        |
| TiO <sub>2</sub> ..               | 1.87   | 0.30   |
| P <sub>2</sub> O <sub>5</sub> ..  | 0.10   | tr.    |
| MnO ..                            | 0.12   | tr.    |
| CO <sub>2</sub> ..                | tr.    | —      |
|                                   | 100.40 | 100.27 |
| Sp. Gr. ..                        | 3.02   | 2.996  |

| Norms.         |       |       |
|----------------|-------|-------|
|                | I.    | II.   |
| Orthoclase ..  | 1.11  | —     |
| Albite ..      | 5.76  | 11.00 |
| Anorthite ..   | 52.26 | 48.65 |
| Diopside ..    | 13.47 | 15.90 |
| Hypersthene .. | 9.10  | 9.85  |
| Olivine ..     | 9.59  | 10.05 |
| Magnetite ..   | 5.57  | 3.25  |
| Ilmenite ..    | 2.58  | 0.61  |
| Apatite ..     | 0.34  | —     |

- I. Hornblende-olivine-norite, (Kedabekase, "III.5."5.4(5)) Por. 63, Parish of Ben Bullen. Anal. G. A. Joplin.  
 II. Gabbro-diorite, (Kedabekase, (II)III.5.(4)5.0) Pikesville, Baltimore County, Maryland. Anal. L. McCay. G. H. Williams, *U.S.G.S.* Bull. 28, 1886, p. 37. In W.T. p. 666, No. 4.

(ii) *Norite and Hornblende-norite.*

These rocks are abundant on the northern, north-western, and north-eastern slopes of Cleared Hill and on the saddle to the east. They are also met with in the gully to the east of this saddle and may continue down as far as the old Mudgee Road. The hybrid type is the commoner, and these masses evidently represent the shattered and partly assimilated remains of the earlier basic complex.

In the hand specimen they are dark, dense, gabbroid rocks and often contain large well-formed crystals of pyroxene. In the hornblende-rich varieties this mineral occurs in "shimmer" plates.

Under the microscope the rock is panidiomorphic granular, sub-ophitic, glomeroporphyritic and/or intergranular. The constituent minerals are plagioclase, mono-

clinic and rhombic pyroxene, iron ores and, in the hybrid type, brown hornblende. Apatite and epidote are often present in small amount, and in one or two cases a little quartz and biotite have been noted.

Pyroxene tends to form clots measuring about 3 mm. These are made up of both monoclinic and rhombic crystals which measure about 1 mm. Irregular grains of iron ore are usually associated, and sometimes dendritic masses of iron ores suggest original olivine. Occasionally the pyroxene masses consist of a single crystal of monoclinic pyroxene.

The rhombic pyroxene, besides forming fairly large crystals in the clot, also occur in smaller stout subidiomorphic prisms or rounded grains between the plagioclase laths. Occasionally the monoclinic mineral occurs in this fashion.

The monoclinic pyroxene is optically positive and  $2V$  is fairly small. The mineral is pale green and non-pleochroic.  $\alpha' = 1.690$ ,  $\gamma' = 1.710$ ;  $Z \wedge C = 40^\circ$ . It therefore appears to be diopsidic in composition.

The hypersthene shows fairly strong pleochroism, with  $X$ =pale rose-pink,  $Y$ =faint yellowish-pink,  $Z$ =greyish-green.  $2V$  is large and the mineral is sometimes optically positive.  $\alpha' = 1.695$ ,  $\gamma' = 1.710$ . The plagioclase shows clearing and mottling and forms tabular crystals or stout laths averaging 2 mm. Occasionally small rounded crystals are developed, and the rock suggests slight recrystallisation.  $\gamma' = 1.569$ . The extinction on sections  $\perp$  to 010 is  $36^\circ$ , the plagioclase, therefore, has the composition  $Ab_{38}An_{62}$ .

In the hybrid types a poikilitic fabric is developed, and large irregular crystals of brown hornblende surround the pyroxenes and penetrate the neighbouring plagioclase. In the normal rocks narrow coronas of amphibole indicate incipient hybridisation.<sup>(9)</sup>

The brown hornblende is optically negative;  $Z \wedge C = 22^\circ$ ;  $\alpha' = 1.662$ ,  $\gamma' = 1.683$ ;  $X$ =light yellow,  $Y$ =dark olive-green,  $Z$ =dark reddish brown ( $Z > Y > X$ ).

Apatite is sporadic in its development and sometimes attains local abundance forming large subidiomorphic prisms.

A little epidote is often present as an alteration product and occasionally a little quartz and biotite are developed in the hybrid.

An analysis of the hybrid type is given in column I below.

|                                   | I.     | II.    | III.  | IV.    | V.    |
|-----------------------------------|--------|--------|-------|--------|-------|
| SiO <sub>2</sub> ..               | 45.36  | 45.31  | 44.52 | 44.04  | 44.40 |
| Al <sub>2</sub> O <sub>3</sub> .. | 21.12  | 19.39  | 21.32 | 20.01  | 20.55 |
| Fe <sub>2</sub> O <sub>3</sub> .. | 4.19   | 5.33   | 5.08  | 4.22   | 6.57  |
| FeO ..                            | 7.01   | 7.81   | 7.19  | 8.61   | 9.26  |
| MgO ..                            | 6.85   | 6.93   | 6.41  | 5.01   | 5.21  |
| CaO ..                            | 12.19  | 11.67  | 12.44 | 11.68  | 11.50 |
| Na <sub>2</sub> O ..              | 0.99   | 1.22   | 1.25  | 1.24   | 1.14  |
| K <sub>2</sub> O ..               | 0.37   | 0.35   | 0.15  | 0.15   | 0.19  |
| H <sub>2</sub> O+ ..              | 0.62   | 0.69   | 0.37  | 1.90   | 1.00  |
| H <sub>2</sub> O- ..              | 0.15   | 0.08   | 0.06  | 0.11   | —     |
| TiO <sub>2</sub> ..               | 1.64   | 1.33   | 1.04  | 2.24   | —     |
| P <sub>2</sub> O <sub>5</sub> ..  | 0.07   | 0.31   | abs.  | 0.52   | —     |
| MnO ..                            | 0.10   | 0.17   | 0.09  | 0.28   | —     |
| CO <sub>2</sub> ..                | abs.   | tr.    | tr.   | abs.   | —     |
| Etc. ..                           | —      | —      | —     | 0.41   | —     |
|                                   | 100.66 | 100.59 | 99.92 | 100.42 | 99.82 |
| Sp. Gr.                           | 2.97   | 3.004  | 3.050 | —      | 3.035 |

*Norms.*

|                     | I.    | II.   | III.  | IV.   | V.    |
|---------------------|-------|-------|-------|-------|-------|
| Quartz ..           | 0.66  | 0.96  | —     | 1.20  | 0.96  |
| Orthoclase          | 2.22  | 1.67  | 0.83  | 1.11  | 1.11  |
| Albite ..           | 8.38  | 9.96  | 10.48 | 12.58 | 9.43  |
| Anorthite           | 51.49 | 46.70 | 52.26 | 47.26 | 50.32 |
| Diopside            | 6.24  | 7.85  | 7.42  | 5.91  | 5.50  |
| Hypers-<br>thene .. | 20.97 | 21.70 | 18.28 | 18.72 | 21.90 |
| Olivine ..          | —     | —     | 1.21  | —     | —     |
| Magnetite           | 6.03  | 7.66  | 7.42  | 6.03  | 9.51  |
| Ilmenite            | 3.92  | 2.43  | 1.98  | 4.26  | —     |
| Apatite             | 0.34  | 0.67  | —     | 1.34  | —     |

I. Hornblende-norite (Corsase near Kedabekase, II(III).5.(4)5.4).  
 Por. 1 Parish of Ben Bullen. Anal. G. A. Joplin.

- II. Hornblende-pyroxene-gabbro or "Reaction"-gabbro (Kedabekase, III.5(4).5.4(5)) Por. 27, Parish of Lowther, Cox's River, Little Hartley. Anal. G. A. Joplin. *Proc. Linn. Soc. N.S.W.*, 1931, 56, p. 53.
- III. Recrystallised Pyroxene-gabbro (leucocratic phase). (Corsase near Kedabekase, II(III).5.(4)5.3"). S. end of Por. 239, Par. Lowther, Little Hartley. Anal. G. A. Joplin. *Ibid.*, 1933, 58, p. 130.
- IV. Hornblende-diorite (Hessose, II(III).5.4(5).''5). Rising Sun, Cecil County, Maryland. Anal. W. F. Hillebrand. A. G. Leonard, *Amer. Geol.*, 1901, 28, p. 146. In W.T., p. 530, No. 19.
- V. Segregation in Norite (Corsase, II(III).5.''5.0). The Bluff, Otago, New Zealand. Anal. L. J. Wild. *Trans. N.Z. Inst.*, 1911 (1912), 44, p. 325. In W.T., p. 552, No. 10.

### (iii) *Recrystallised Gabbros.*

About twelve small patches of recrystallised gabbro are recorded in the Earlier Basic Complex, and among these are represented (a) types that are unaffected by hybridisation, (b) types that are slightly acidified, and (c) types that are definite hybrids containing hornblende or biotite or both.

These rocks have been collected in the depression N.E. of Little Jew's Mt. near the Old Mudgee Road, near the summit of Cleared Hill, just north of the road in Por. 65, and a few boulders of the hybrid type occur among the quarry *débris* on Por. 45, 46 and 47.

In the hand specimen these are fine-grained dense rocks and hornblende may usually be discerned in the hybrids. The blocks found in the limestone quarry are peculiar. They are often veined with the later quartz-mica-diorite, and are believed to have been tongues of the earlier complex injected into the limestone. Some show limestone contamination as well as hybridisation from the later magma. These rocks contain large crystals of brown hornblende measuring up to 14 mm. and often altered to criss-cross flakes of biotite, and in addition biotite may form perfect idiomorphic crystals up to 10 mm. across. This rock has been figured in an earlier publication.<sup>(9)</sup>

Under the microscope the recrystallised gabbros show a granoblastic and porphyroblastic structure, and in addition the hybrid types contain a poikilitic development of hornblende and/or biotite. The porphyroblasts may be either plagioclase or augite and the ground mass consists of small granules of augite, hypersthene and iron ore, and granules and small laths of plagioclase felspar. The

laths and the felspar porphyroblasts are indented by the smaller granular minerals and present sutured boundaries.

The plagioclase is often quite limpid, and, in the more feldspathic types, may contain minute granular inclusions of pyroxene and iron ores. These small inclusions are grouped in the centre of the crystal and are often zonally arranged (see Figs.).<sup>(8)</sup> <sup>(9)</sup> A glomero-porphyrific grouping of the felspar porphyroblasts is also common. The plagioclase occasionally shows inverted zoning, but zoning is not a common feature. The extinction measured on sections  $\perp$  to 010 is  $26^\circ$ ,  $\alpha' = 1.552$ ,  $\gamma' = 1.560$  and the composition is therefore  $\text{Ab}_{53}\text{An}_{47}$ . In the hybrid types the felspars often show mottling and may be bordered with a plagioclase of the composition  $\text{Ab}_{64}\text{An}_{46}$ .

Hypersthene forms small subidiomorphic prisms or rounded grains which usually measure about 0.8 mm. Pleochroism is relatively strong,  $\alpha' = 1.685$ ,  $\gamma' = 1.693$ .

Augite has a similar habit to the hypersthene, and in the rocks containing porphyroblasts of this mineral it forms sub-idiomorphic crystals measuring 3 mm.,  $Z \wedge C = 46^\circ$ ,  $\alpha' = 1.680$ ,  $\gamma' = 1.705$ .

Hornblende is present in the hybrid types and may occur as large independent crystals or as poikilitic crystals including iron ores, pyroxenes and felspar. Pyroxene porphyroblasts often show a border of brown hornblende. The mineral is strongly pleochroic, with  $X$ =pale golden yellow,  $Y$ =yellowish brown,  $Z$ =reddish brown ( $Z > Y > X$ ),  $Z \wedge C = 24^\circ$ ,  $\alpha' = 1.662$ ,  $\gamma' = 1.687$ .

Biotite also occurs as independent or highly poikilitic crystals and may sometimes form criss-cross flakes pseudomorphing hornblende  $\beta = 1.625$ ,  $X$ =golden yellow,  $Y$ =golden brown,  $Z$ =reddish brown.

Iron ores are fairly abundant and usually form rounded grains associated with the ferromagnesian minerals. Apatite is usually present in small amount.

An analysis of a feldspathic type of unhybridised recrystallised gabbro is given in column I, p. 78.

#### (iv) *Quartz-bearing Pyroxene-diorite or Basified Diorite.*

In the hand specimen the rock has the appearance of a typical diorite consisting of hornblende and plagioclase. The grain size is medium and the density fairly high.

Under the microscope the rock is hypidiomorphic to panidiomorphic granular, and the fabric is subophitic to poikilitic. The grain size averages about 1.5 mm., and

|                                      | I.     | II.    | III.   | IV.    |
|--------------------------------------|--------|--------|--------|--------|
| SiO <sub>2</sub> .. ..               | 48.42  | 47.23  | 47.41  | 50.50  |
| Al <sub>2</sub> O <sub>3</sub> .. .. | 21.53  | 18.49  | 20.40  | 21.07  |
| Fe <sub>2</sub> O <sub>3</sub> .. .. | 3.09   | 6.14   | 3.35   | 1.85   |
| FeO .. ..                            | 7.84   | 8.79   | 7.24   | 3.62   |
| MgO .. ..                            | 4.96   | 3.92   | 7.53   | 5.26   |
| CaO .. ..                            | 9.12   | 7.89   | 9.70   | 13.20  |
| Na <sub>2</sub> O .. ..              | 2.43   | 2.84   | 2.14   | 2.09   |
| K <sub>2</sub> O .. ..               | 0.39   | 0.51   | 0.42   | 0.36   |
| H <sub>2</sub> O+ .. ..              | 0.25   | 1.26   | 1.20   | 0.92   |
| H <sub>2</sub> O- .. ..              | 0.09   | 0.04   | —      | none   |
| TiO <sub>2</sub> .. ..               | 1.41   | 2.04   | 1.11   | 0.29   |
| P <sub>2</sub> O <sub>5</sub> .. ..  | 0.39   | 0.14   | —      | 0.36   |
| MnO .. ..                            | 0.11   | 0.63   | —      | —      |
| CO <sub>2</sub> .. ..                | abs.   | 0.11   | —      | 0.32   |
| Etc. .. ..                           | —      | 0.18   | —      | 0.33   |
|                                      | 100.03 | 100.21 | 100.50 | 100.17 |
| Sp. Gr. .. ..                        | 2.98   | —      | —      | —      |

## Norms.

|                   | I.    | II.   | III.  | IV.   |
|-------------------|-------|-------|-------|-------|
| Quartz .. ..      | 2.76  | 2.88  | —     | 3.24  |
| Orthoclase .. ..  | 2.22  | 2.78  | 2.22  | 2.22  |
| Albite .. ..      | 20.44 | 24.10 | 17.82 | 17.82 |
| Anorthite .. ..   | 42.81 | 36.14 | 45.04 | 46.70 |
| Corundum .. ..    | 1.43  | —     | —     | —     |
| Diopside .. ..    | —     | 1.83  | 2.48  | 12.91 |
| Olivine .. ..     | —     | —     | 4.23  | —     |
| Hypersthene .. .. | 21.77 | 17.75 | 20.47 | 11.50 |
| Magnetite .. ..   | 4.41  | 8.82  | 4.87  | 2.78  |
| Ilmenite .. ..    | 2.74  | 3.95  | 2.13  | 0.61  |
| Apatite .. ..     | 1.01  | 0.34  | —     | 1.01  |

I. Recrystallised Pyroxene-gabbro (Hessose, II.5.4.(4)5). Por. 1, Parish of Ben Bullen. Anal. G. A. Joplin.

II. Beerbachite (Hessose, II".5.4.(4)5). Samoyed Urals, Russia. Anal. H. Bucklund. *Mem. Imp. Ac. Sci. St. Pet.*, 1912, 38, No. 3, p. 30. In W.T. p. 542, No. 113.

III. Gabbro inclusion in Basalt (Hessose, II(III).5.4.(4)5). Schluckenau, Bohemia. Anal. C. v. John. *Jb. G.R.-A., Wien*, 1903, 52, p. 150. In W.T. p. 540, No. 98.

IV. Gabbro (Hessose, II.5.4''.(4)5). Seeheimer Bruch, Odenwald. Anal. G. Butzbach. G. Klemm, *Nb. Ver. Erdk.* (4), 1906, 27, 12. In W.T. p. 540, No. 88.

the constituent minerals are plagioclase, hornblende, augite, biotite, quartz, iron ore, apatite, and a little prehnite.

The plagioclase forms irregularly bounded laths and is usually zoned. The greater part of the plagioclase has  $\alpha' = 1.552$ ,  $\gamma' = 1.562$ , it is optically positive and the extinction on sections  $\perp$  to 010 is  $30^\circ$ . This indicates  $\text{Ab}_{48}\text{An}_{52}$ . The outer rim of many of these crystals has an extinction of  $18^\circ$  and appears to be andesine ( $\text{Ab}_{62}\text{An}_{38}$ ).

The hornblende is greenish-brown in colour and forms sub-idiomorphic prisms about 1.5 mm. in length.  $Z$ =olive green to brownish-green,  $Y$ =olive-green to brownish-green,  $X$ =yellowish-green to brownish-yellow, ( $Z > Y > X$ );  $Z \wedge C = 18^\circ$ ,  $\alpha' = 1.660$ ,  $\gamma' = 1.685$ .

Biotite is not abundant but shows local concentrations.  $X$ =golden-yellow,  $Y$ =reddish-brown,  $Z$ =chocolate-brown ( $Z > Y > X$ ). This mineral shows alteration into chlorite and sometimes to epidote. Occasionally lens-like masses of prehnite occur between the cleavages of the biotite. The mineral is biaxial and positive;  $\alpha' = 1.615$ ,  $\gamma' = 1.630$ ; and the elongation is negative; extinction is straight; and a cleavage is developed parallel to the elongation of the lenses and therefore parallel to the cleavage of the biotite. The writer recognised a mineral with a similar occurrence in the quartz-mica-diorites at Hartley,<sup>(7)</sup> but owing to the paucity of the material it could not be satisfactorily determined. Stillwell<sup>(15)</sup> described lawsonite occurring in an exactly similar manner in the biotite of the actinolite-schists of Adélie Land, and it was thus suggested that the Hartley mineral might also be lawsonite.<sup>(7)</sup> It is now believed that it is prehnite, as it appears to be identical with the Ben Bullen mineral. Friedlaender and Niggli<sup>(5)</sup> have described and figured lenses of phenacite in the biotite of the granodiorites of the Voges.\*

\* H. von Eckermann (*Geol. Fören. Stockholm Förhandl.*, 1936, 80, 255) has recently described an unidentified mineral with a higher R.I. occurring as lenses in chlorite.



Augite forms subidiomorphic prisms, but usually occurs as cores within the hornblende. It is often uraltised.

All three ferromagnesian minerals may be highly poikilitic and contain inclusions of plagioclase, apatite, and iron ores. Small (0.7 mm.) quartz grains are interstitial and in a few slides a little orthoclase has been noted.

An analysis of this type is given in column I below.

|                                   | I.     | II.    | III.   | IV.    | V.     | VI.    |
|-----------------------------------|--------|--------|--------|--------|--------|--------|
| SiO <sub>2</sub> ..               | 47.95  | 48.78  | 46.49  | 52.41  | 49.80  | 47.64  |
| Al <sub>2</sub> O <sub>3</sub> .. | 21.20  | 22.07  | 19.22  | 20.11  | 17.77  | 19.98  |
| Fe <sub>2</sub> O <sub>3</sub> .. | 1.69   | 1.92   | 6.68   | 4.18   | 2.29   | 4.83   |
| FeO ..                            | 8.85   | 7.73   | 6.02   | 5.59   | 8.75   | 7.26   |
| MgO ..                            | 4.95   | 5.22   | 5.89   | 4.12   | 5.67   | 7.14   |
| CaO ..                            | 9.50   | 9.67   | 10.88  | 9.06   | 8.85   | 9.62   |
| Na <sub>2</sub> O ..              | 1.70   | 1.81   | 2.16   | 2.28   | 1.48   | 1.23   |
| K <sub>2</sub> O ..               | 0.76   | 1.17   | 0.65   | 0.88   | 0.48   | 1.03   |
| H <sub>2</sub> O+ ..              | 0.60   | 1.68   | 0.96   | 0.36   | 2.62   | 0.12   |
| H <sub>2</sub> O- ..              | 0.02   | —      | 0.17   | 0.16   | 1.04   | —      |
| TiO <sub>2</sub> ..               | 1.59   | 0.37   | 0.92   | 0.78   | 1.56   | 1.20   |
| P <sub>2</sub> O <sub>5</sub> ..  | 0.38   | 0.44   | 0.40   | 0.32   | tr.    | —      |
| MnO ..                            | 0.18   | tr.    | 0.20   | 0.19   | —      | —      |
| CO <sub>2</sub> ..                | 0.74   | —      | tr.    | tr.    | —      | 0.28   |
|                                   | 100.11 | 100.86 | 100.64 | 100.46 | 100.31 | 100.43 |
| Sp. Gr. ..                        | 2.92   | —      | 2.967  | 2.836  | 2.932  | 2.979  |

*Norms.*

|             | I.    | II.   | III.  | IV.   | V.    | VI.   |
|-------------|-------|-------|-------|-------|-------|-------|
| Quartz ..   | 4.50  | 1.20  | 0.96  | 8.34  | 7.38  | 2.28  |
| Orthoclase  | 5.00  | 6.67  | 3.34  | 5.56  | 2.78  | 6.12  |
| Albite ..   | 14.15 | 15.20 | 18.34 | 19.39 | 12.58 | 10.48 |
| Anorthite   | 40.31 | 45.31 | 40.87 | 41.70 | 40.31 | 45.59 |
| Corundum    | 2.75  | 1.43  | —     | —     | —     | —     |
| Diopside .. | —     | —     | 8.64  | 1.11  | 2.97  | 1.57  |
| Hypersthene | 24.81 | 24.98 | 14.93 | 15.71 | 24.36 | 24.53 |
| Magnetite   | 2.55  | 2.78  | 9.74  | 6.03  | 3.25  | 6.96  |
| Ilmenite .. | 3.04  | 0.76  | 1.67  | 1.52  | 3.04  | 2.28  |
| Apatite ..  | 1.01  | 1.01  | 1.01  | 0.67  | —     | —     |
| Calcite ..  | 1.60  | —     | —     | —     | —     | —     |

- I. Quartz-bearing Pyroxene-diorite or Basified Diorite (Hessose, II''.'5.4.4.). Head of Spring Gully, Por. 1, Parish of Ben Bullen. Anal. G. A. Joplin.
- II. Gabbro (Hessose, II.5.4.4.). Near Abu Uruf, Kordofan. Anal. Sprockhoff. G. Linck, *N.J.B.*, B., 1903, 17, p. 412. In W.T. p. 544, No. 118.
- III. Diorite-gabbro (Hessose, II(III).5.4.4(5)). Moyne Farm, Little Hartley. Anal. G. A. Joplin. *Proc. Linn. Soc. N.S.W.*, 1931, 51, p. 41.
- IV. Quartz-mica-diorite (Hessose, II.(4)5.4.4.). Marriott's Creek, Cox's River Intrusion, Little Hartley. Anal. G. A. Joplin. *Ibid.*, p. 38.
- V. Diabase (Hessose, II(III).(4)5.4''.4.). Auchinstarry, Kilsyth, Dumbartonshire, Scotland. Anal. D. P. Macdonald. G. W. Tyrrell, *Geol. Mag.*, 1909, (5), 6, p. 361. In W.T. p. 538, No. 75.
- VI. Diabase (Hessose, II(III).5.4''.(3)4.). Förväxlings Point, Spitzbergen. Anal. H. Buckland. H. Buckland, *Ref. N.J.*, 1911, 11, p. 243. In W.T. p. 538, No. 72.

#### The Later Intrusion and Included Xenoliths.

##### (i) *Quartz-mica-diorite.*

The narrow north-south strip lying to the west of the main mass consists of quartz-mica-diorite, and this type also makes up the bulk of the north-western part of the intrusion as well as its southern lobe. The southern outcrop is slightly more acid but is essentially the same rock.

In the hand specimen the rock is a typical diorite consisting of about equal proportions of light and dark minerals. The grain size is usually medium, but fairly coarse types may occur. Small, dark, fine-grained xenoliths are very common in the quartz-mica-diorite.

Under the microscope the rock is seen to be hypidiomorphic granular and the fabric is sub-ophitic to poikilitic. The grain size averages about 2 mm., but occasionally the rock is slightly porphyritic and plagioclase phenocrysts may measure up to 3 mm., whilst the ground mass averages 0.5 mm.

The constituent minerals are plagioclase, hornblende, biotite, quartz, iron ores, apatite and a little prehnite, epidote, chlorite, and white mica. A small quantity of orthoclase has been noted in the more acid varieties, and the presence of uraltite suggests original pyroxene in a few of the slides.

Plagioclase occurs in tabular crystals or in laths and averages 1 to 2 mm., but two generations are sometimes developed. The refractive indices are variable; the

mineral may be either positive or negative and extinction angles measured on sections  $\perp$  to 010 vary from  $27^\circ$  to  $21^\circ$ . The feldspar is therefore andesine and ranges in different specimens from  $\text{Ab}_{52}\text{An}_{48}$  to  $\text{Ab}_{59}\text{An}_{41}$ . The plagioclase phenocrysts are often highly zoned and range from  $\text{Ab}_{49}\text{An}_{51}$  to  $\text{Ab}_{63}\text{An}_{37}$ .

Hornblende is developed in subidiomorphic prisms (averaging two mm.) or in poikilitic crystals wrapping and enclosing plagioclase. It is optically negative;  $Z \wedge C = 19^\circ$ ;  $X$ =pale yellowish-green,  $Y$ =olive-green,  $Z$ =dark bluish-green ( $Z > Y > X$ ). Simple and polysynthetic twinning are often developed on 100. Refractive indices vary in the different specimens from  $\alpha' = 1.652$ – $1.665$ ,  $\gamma' = 1.681$ – $1.687$ .

Biotite is usually abundant, but may vary considerably in amount. In one case it completely takes the place of hornblende, and in another it is entirely absent. It occurs in ragged flakes from 5 to 2 mm.  $X$ =golden-yellow,  $Y$ =light brown or reddish-brown,  $Z$ =chocolate-brown, ( $Z > Y > X$ );  $\beta' = 1.600$ . The mineral shows alteration into chlorite and epidote and lenses of prehnite are fairly common.

Quartz occurs in interstitial allotriomorphic grains from three mm. to less than 0.5 mm. It is more abundant in the rocks of the southern lobe of the intrusion. Iron ores are always accessory and apatite forms small, acicular inclusions.

An analysis of this type is given in Column I below.

|                            | I.     | II.    | III.   | IV.    | V.     |
|----------------------------|--------|--------|--------|--------|--------|
| $\text{SiO}_2$ ..          | 55.30  | 55.42  | 54.37  | 58.30  | 57.15  |
| $\text{Al}_2\text{O}_3$ .. | 20.87  | 21.35  | 19.64  | 19.43  | 19.26  |
| $\text{Fe}_2\text{O}_3$ .. | 3.62   | 3.37   | 4.30   | 4.40   | 1.36   |
| $\text{FeO}$ ..            | 5.20   | 4.87   | 4.87   | 3.33   | 4.17   |
| $\text{MgO}$ ..            | 2.75   | 3.87   | 2.94   | 2.64   | 3.58   |
| $\text{CaO}$ ..            | 7.44   | 7.51   | 8.07   | 7.46   | 7.13   |
| $\text{Na}_2\text{O}$ ..   | 2.49   | 2.94   | 2.55   | 3.07   | 2.88   |
| $\text{K}_2\text{O}$ ..    | 0.82   | 0.68   | 1.01   | 0.88   | 1.10   |
| $\text{H}_2\text{O}+$ ..   | 0.76   | 0.37   | 0.96   | 0.37   | 1.41   |
| $\text{H}_2\text{O}-$ ..   | 0.08   | —      | 0.11   | —      | 0.68   |
| $\text{TiO}_2$ ..          | 0.90   | 0.33   | 1.14   | 0.49   | 0.84   |
| $\text{P}_2\text{O}_5$ ..  | 0.41   | tr.    | 0.34   | 0.22   | 0.10   |
| $\text{MnO}$ ..            | 0.10   | —      | 0.07   | —      | 0.42   |
| Etc. ..                    | —      | —      | —      | —      | 0.12   |
|                            | 100.74 | 100.71 | 100.37 | 100.57 | 100.20 |
| Sp. Gr.                    | 2.83   | —      | 2.861  | —      | —      |

*Norms.*

|                    | I.    | II.   | III.  | IV.   | V.    |
|--------------------|-------|-------|-------|-------|-------|
| Quartz ..          | 16.44 | 11.52 | 13.14 | 17.34 | 13.02 |
| Orthoclase         | 5.00  | 3.89  | 6.12  | 5.00  | 6.67  |
| Albite ..          | 20.96 | 24.63 | 20.96 | 26.20 | 24.63 |
| Anorthite          | 34.19 | 37.25 | 38.09 | 35.03 | 34.47 |
| Corundum           | 3.37  | 2.14  | 0.41  | 0.51  | 0.61  |
| Hypers-<br>thene.. | 12.05 | 15.38 | 11.00 | 8.18  | 14.18 |
| Magnetite          | 5.34  | 4.87  | 6.26  | 6.50  | 2.09  |
| Ilmenite           | 1.67  | 0.61  | 2.13  | 0.91  | 1.67  |
| Apatite            | 1.01  | —     | 0.67  | 0.67  | 0.34  |

- I. Quartz-mica-diorite (Bandose, II.4.4.4''). Por. 57/58, Parish of Ben Bullen. Anal. G. A. Joplin.
- II. Diabase Inclusion in Andesite (Bandose, II.4(5).4.4(5)). Mount Pélee, Martinique, W. Indies. Anal. A. Pisani. A. Lacroix, Mt. Pélee, 1904, p. 573. In W.T. p. 410, No. 36.
- III. Quartz-mica-diorite (Bandose, II.4''4.4.). Moyne Farm, Little Hartley. Anal. G. A. Joplin. *Proc. Linn. Soc. N.S.W.*, 1931, 56, p. 37.
- IV. Andesilaborite (Bandose, (I)II.4.''4.4''). Carbet, Martinique, West Indies. Anal. A. Pisani. A. Lacroix, Mt. Pélee, 1904, p. 573. In W.T. p. 410, No. 31.
- V. Andesite (Bandose, II.4''.''4.4.). Thames Mine, Hauraki, Auckland, New Zealand. Anal. J. S. MacLaurin. C. Frazer, *N.Z.G.S.*, Bull. 10, 1910, p. 24. In W.T. p. 418, No. 88.

(ii) *Basic Xenoliths.*

Basic xenoliths of igneous origin occur throughout the quartz-mica-diorite mass and are particularly abundant on Jew's Creek. They are always darker and finer grained than their host and usually occur in small rounded patches which may measure up to three inches in diameter. Under the microscope they present a great variety of structures, grain size and mineral content, and it is believed that this variation is largely due to the degree of contamination and incorporation which each has attained. Some of the xenoliths show evidence of an earlier recrystallisation, and granoblastic and sieve structures are sometimes preserved. Other xenoliths show highly poikilitic plates of hornblende and biotite which appear to be due to hybridisation, and in those that are beginning to develop a coarser grain size, and to become completely incorporated

in the quartz-mica-diorite, large crystals of plagioclase and biotite are developed.<sup>(14)</sup>

The rock may contain hornblende to the exclusion of biotite, or *vice versa*, and many contain about equal proportions of these two minerals. Some of the hornblende occurs in subidiomorphic prisms which are very slender and have sutured boundaries. They average 1 mm. in length. The hornblende is a green variety with  $X =$  yellowish-green,  $Y =$  dark olive-green,  $Z =$  dark bluish-green; it is often twinned;  $Z \wedge C = 18^\circ$ ; and alteration to chlorite is frequent.

Biotite occurs in small flakes and/or in large poikilitic sheets. In those rocks which are almost incorporated, biotite occurs in large flakes comparable to that of the diorite and the poikilitic structure is not well marked. The poikilitic flakes and the smaller units both have fairly high refractive indices ( $\alpha' = 1.622$ ,  $\gamma' = 1.665$ );  $X =$  pale yellowish-brown,  $Y =$  deep reddish-brown,  $Z =$  very dark reddish-brown.

Plagioclase forms small laths, irregular grains or small tabular crystals, and averages about 0.25 mm. Larger tabular crystals are present in the more highly disintegrated types, and this feldspar appears to have the same composition as that of the host. The composition of the smaller crystals is variable, and they often show basic cores ( $Ab_{48}An_{52}$ ) and more acid rims ( $Ab_{63}An_{37}$ ). Alteration to epidote or sericite is frequent.

No analysis of a xenolith has been made, as they vary a good deal in composition and in degree of contamination, and it is fairly certain that there has been mechanical addition of material from the surrounding magma.

#### Dykes and Veins.

##### (i) *Hornblende-lamprophyres.*

A small dyke of hornblende-lamprophyre strikes across the creek near the S.W. corner of Por. 87, and veins measuring only about an inch in width are occasionally met with in different parts of the igneous mass. One such vein occurs in the Cleared Hill Quarry and the development of epidote and clinozoisite suggests limestone contamination.

The rocks are porphyritic and contain slender idiomorphic or subidiomorphic prisms of hornblende which may measure up to 2.5 mm., and tabular crystals of plagioclase averaging

0.5 mm. These are set in a fine-grained ground mass of plagioclase and hornblende which averages about 0.1 mm.

The hornblende phenocrysts sometimes form groups and are often altered to uraalite. A peculiar brown blotching is also common, and the crystals may have a brown outer rim.

The large plagioclase crystals are frequently zoned, and are free from alteration products, whilst the small laths of the ground mass show alteration.

Sphene is moderately abundant and may form irregular grains. Biotite may or may not be developed, and iron ores occur as small inclusions.

In the smaller veins the slender hornblende prisms and felspar laths are roughly parallel to the length of the vein.

#### (ii) *Aplites*.

A few veins of aplite occur in different parts of the igneous mass, the largest being about six inches wide and outcropping for a few feet in the cutting of the quarry tramline on Por. 63. The rock appears to consist only of quartz and felspar, but it is much altered and has not been sectioned.

### 4. PETROGENESIS.

#### Chemical Discussion and Comparison with Hartley.

The analyses numbered I to V on page 88 represent hybrid, recrystallised and unmodified rocks from Ben Bullen, but it will be seen that there is a graduation in chemical and normative composition, and that all these types take their places on a variation diagram characteristic of a calcic series. (Fig. 2.)

With the exception of the relative proportions of the alkalis and iron oxides there is a very close correspondence between the composition of the recrystallised gabbro and that of the basified diorite. It seems evident that the recrystallised rock is the most acid member of the earlier complex, and that it has not suffered hybridisation. Assuming this to be the case, it is evident that the earlier intrusion was relatively richer in iron and poorer in potash. The hybrids of the earlier complex do not show this difference, and it is probable that the addition of potash has been an important factor in hybridisation.

The Ben Bullen series as a whole is characterised by the fact that FeO is always higher than MgO, and in this it compares with the Hartley complex, which is illustrated by analyses A to F. Like the Hartley series the Ben Bullen

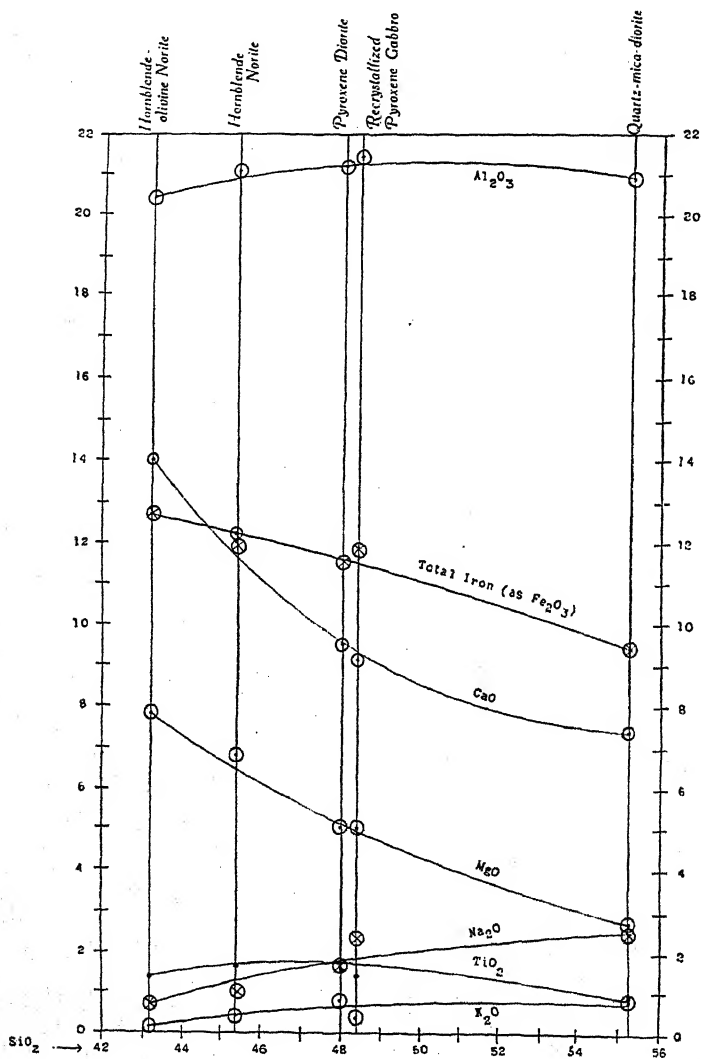


Fig. 2.—Variation diagram of Ben Bullen Plutonic Complex.

rocks also show high alumina, but in the latter area it is consistently higher than at Hartley. Titania is also a little higher at Ben Bullen, though it is present in appreciable amounts in the Hartley complex and is apparently characteristic of all intrusions of the Kanimbla epoch<sup>(1)</sup> and of Late-Palaeozoic age.<sup>(2)</sup>

A comparison of the Ben Bullen and Hartley analyses also shows that  $\text{Fe}_2\text{O}_3$  and  $\text{Na}_2\text{O}$  are higher at Hartley, but it seems likely that these minor differences are quite local and may be due to differentiation in place. Apart from the dissimilarities pointed out above, there is a striking resemblance between the two complexes, and the slight differences might be expected in any series of analyses of consanguineous rocks outcropping over a wide area. It seems evident, therefore, that the Hartley and Ben Bullen magmas arose from the same magma reservoir and that differentiation *in situ* caused slightly different trends. Ben Bullen lies about eighteen miles N.N.W. of Hartley, and this assumption would thus suggest a northerly extension of the Hartley-Bathurst batholith.

#### Possible Origin of the Various Rock Types.

It seems evident that there were two injections of partial magma in the Ben Bullen area—first, norite, and secondly, quartz-mica-diorite. The second intrusion partly surrounds the first, and the present basic mass possibly represents a portion of the roof of the second magma chamber. The field occurrence points to a shattering and partial assimilation of the earlier complex by the later more acid magma.

Reference to the petrography will show that the earlier complex consisted originally of three main types—olivine-norite, norite or hypersthene-gabbro and a more acid type of gabbro. The latter is recrystallised, and, as only one analysis has been made of this type, it is uncertain whether all the recrystallised rocks, unaffected by hybridisation, are of comparable acidity, though this is not an unreasonable assumption.

These three types possibly arose from the noritic magma by differentiation *in situ*. The second intrusion of partial magma then occurred and the earlier complex was partially recrystallised. The reason for this incomplete or selective recrystallisation is rather obscure, but two explanations suggest themselves. First, the rocks which are now recrystallised may have been immediately adjacent to the



|                                   | I.     | A.    | B.    | C.     | II.    | D.     | III.   | IV.    | E.     | F.     | V.     |
|-----------------------------------|--------|-------|-------|--------|--------|--------|--------|--------|--------|--------|--------|
| SiO <sub>2</sub> ..               | 43.15  | 44.52 | 44.79 | 45.31  | 45.36  | 46.49  | 47.95  | 48.42  | 52.41  | 54.37  | 55.30  |
| Al <sub>2</sub> O <sub>3</sub> .. | 20.45  | 21.32 | 19.56 | 19.39  | 21.12  | 19.22  | 21.20  | 21.53  | 20.11  | 19.64  | 20.87  |
| Fe <sub>2</sub> O <sub>3</sub> .. | 3.79   | 5.08  | 6.01  | 5.33   | 4.19   | 6.68   | 1.69   | 3.09   | 4.18   | 4.30   | 3.62   |
| FeO ..                            | 7.98   | 7.19  | 7.79  | 7.81   | 7.01   | 6.02   | 8.85   | 7.84   | 5.59   | 4.87   | 5.20   |
| MgO ..                            | 7.82   | 6.44  | 6.16  | 6.93   | 6.85   | 5.89   | 4.95   | 4.96   | 4.12   | 2.94   | 2.75   |
| CaO ..                            | 14.03  | 12.44 | 11.81 | 11.67  | 12.19  | 10.88  | 9.50   | 9.12   | 9.06   | 8.07   | 7.44   |
| Na <sub>2</sub> O ..              | 0.71   | 1.25  | 1.21  | 1.22   | 0.99   | 2.16   | 1.70   | 2.43   | 2.28   | 2.55   | 2.49   |
| K <sub>2</sub> O ..               | 0.15   | 0.15  | 0.06  | 0.35   | 0.37   | 0.65   | 0.76   | 0.39   | 0.88   | 1.01   | 0.82   |
| H <sub>2</sub> O + ..             | 0.58   | 0.37  | 0.64  | 0.69   | 0.62   | 0.96   | 0.60   | 0.25   | 0.36   | 0.96   | 0.76   |
| H <sub>2</sub> O - ..             | 0.15   | 0.06  | 0.10  | 0.08   | 0.15   | 0.17   | 0.02   | 0.09   | 0.16   | 0.11   | 0.08   |
| TiO <sub>2</sub> ..               | 1.37   | 1.04  | 1.14  | 1.33   | 1.64   | 0.92   | 1.59   | 1.41   | 0.78   | 1.14   | 0.90   |
| P <sub>2</sub> O <sub>5</sub> ..  | 0.10   | abs.  | 0.18  | 0.31   | 0.07   | 0.40   | 0.38   | 0.39   | 0.32   | 0.34   | 0.41   |
| MnO ..                            | 0.12   | 0.09  | 0.15  | 0.17   | 0.10   | 0.20   | 0.18   | 0.11   | 0.19   | 0.07   | 0.10   |
| CO <sub>2</sub> ..                | tr.    | tr.   | tr.   | tr.    | abs.   | tr.    | 0.74   | abs.   | tr.    | abs.   | abs.   |
|                                   | 100.40 | 99.92 | 99.60 | 100.59 | 100.66 | 100.64 | 100.11 | 100.03 | 100.46 | 100.37 | 100.74 |
| Sp. Gr. ..                        | 3.02   | 3.050 | 3.055 | 3.004  | 2.97   | 2.967  | 2.92   | 2.98   | 2.836  | 2.861  | 2.83   |

## Norms.

|                         | I.         | A.                           | B.                           | C.         | II.                          | D.      | III.    | IV.     | E.                        | F.      | V.      |
|-------------------------|------------|------------------------------|------------------------------|------------|------------------------------|---------|---------|---------|---------------------------|---------|---------|
| Quartz                  | —          | —                            | 2.04                         | 0.96       | 0.66                         | 0.96    | 4.50    | 2.76    | 8.34                      | 13.14   | 16.44   |
| Orthoclase              | 1.11       | 0.83                         | 0.56                         | 1.67       | 2.22                         | 3.34    | 5.00    | 2.22    | 5.56                      | 6.12    | 5.00    |
| Albite                  | 5.76       | 10.48                        | 9.96                         | 9.96       | 8.38                         | 18.34   | 14.15   | 20.44   | 19.39                     | 20.96   | 20.96   |
| Anorthite               | 52.26      | 52.26                        | 47.82                        | 46.70      | 51.49                        | 40.87   | 40.31   | 42.81   | 41.70                     | 38.09   | 34.19   |
| Corundum                | —          | —                            | —                            | —          | —                            | —       | 2.75    | 1.43    | —                         | 0.41    | 3.37    |
| Diopside                | 13.47      | 7.42                         | 8.10                         | 7.85       | 6.24                         | 8.64    | —       | —       | 1.11                      | —       | —       |
| Hypsthene               | 9.10       | 18.28                        | 19.14                        | 21.70      | 20.97                        | 14.93   | 24.81   | 21.77   | 15.71                     | 11.00   | 12.05   |
| Olivine                 | 9.59       | 1.21                         | —                            | —          | —                            | —       | —       | —       | —                         | —       | —       |
| Magnetite               | 5.57       | 7.42                         | 8.82                         | 7.66       | 6.03                         | 9.74    | 2.55    | 4.41    | 6.03                      | 6.26    | 5.34    |
| Ilmenite                | 2.58       | 1.98                         | 2.13                         | 2.43       | 3.92                         | 1.67    | 3.04    | 2.74    | 1.52                      | 2.13    | 1.67    |
| Apatite                 | 0.34       | —                            | 0.34                         | 0.67       | 0.34                         | 1.01    | 1.01    | 1.01    | 0.67                      | 0.67    | 1.01    |
| Calcite                 | —          | —                            | —                            | —          | —                            | —       | 1.60    | —       | —                         | —       | —       |
| Class                   | III        | II(III)                      | (II)III                      | III        | II(III)                      | II(III) | II"     | II      | II                        | II      | II      |
| Order                   | 5          | 5                            | 5                            | 5(4)       | 5                            | 5       | "5      | 5       | (4)5                      | 4"      | 4       |
| Rang                    | "5         | (4)5                         | (4)5                         | 5          | (4)5                         | 4       | 4       | 4       | 4                         | 4       | 4       |
| Subrang                 | 4(5)       | 3                            | 5                            | 4(5)       | 4                            | 4(5)    | 4       | (4)5    | 4                         | 4       | 4"      |
| M a g m a t i c<br>name | Kedabekase | Corsase<br>nr.<br>Kedabekase | Kedabekase<br>nr.<br>Corsase | Kedabekase | Corsase<br>nr.<br>Kedabekase | Hessose | Hessose | Hessose | Hessose<br>nr.<br>Bandose | Bandose | Bandose |

- I. Olivine-norite, Por. 63, Parish of Ben Bullen. Anal. G. A. Joplin.
- A. Recrystallised Pyroxene-gabbro (leucocratic phase), Cox's River Intrusion, Little Hartley. Anal. G. A. Joplin. *Proc. Linn. Soc. N.S.W.*, 1933, 53.
- B. Recrystallised Pyroxene-gabbro (normal type), Cox's River Intrusion, Little Hartley. Anal. G. A. Joplin. *Ibid.*
- C. "Reaction"-gabbro or Hornblende-pyroxene-gabbro, Cox's River Intrusion, Little Hartley. Anal. G. A. Joplin. *Ibid.*, 1931, 56.
- II. Hornblende-norite, Por. 1, Parish of Ben Bullen. Anal. G. A. Joplin.
- D. Diorite-gabbro, Moyne Farm, Little Hartley. Anal. G. A. Joplin. *Ibid.*
- III. Quartz-bearing Pyroxene-diorite or Basified Diorite. Head of Spring Gully, Ben Bullen. Anal. G. A. Joplin.
- IV. Recrystallised Pyroxene-gabbro, Por. 1, Parish of Ben Bullen. Anal. G. A. Joplin.
- E. Quartz-mica-diorite, Cox's River Intrusion, Little Hartley. Anal. G. A. Joplin. *Ibid.*
- F. Quartz-mica-diorite, Moyne Farm, Little Hartley. Anal. G. A. Joplin. *Ibid.*
- V. Quartz-mica-diorite, Pors. 57/58, Parish of Ben Bullen. Anal. G. A. Joplin.

uprising magma, and at a later stage they were rifted off and scattered in the magma. Rocks that had escaped this first impress of metamorphism would therefore be brought into contact with the magma when the temperature was such that hybridization could take place, but not recrystallisation. Some of the recrystallised rocks may have escaped hybridisation on account of their geographical position. Secondly, it is possible that recrystallisation was selective. These rocks, being of a more acid type, may have contained hornblende which was unstable at the initial temperature of the second intrusion. The hornblende would then break up into augite, hypersthene, and anorthite<sup>(8)</sup> and crystalloblastic structures would be developed. It is likely that some of the hornblende-norites are of slightly more acid type and represent the original acid differentiate which has escaped recrystallisation.

The quartz-mica-diorite magma then began to react with the solid rocks of the earlier complex, and the olivine-norite thus became a hornblende-olivine-norite, and the norite a hornblende-norite. Some of the recrystallised rocks were also made over to hornblende-bearing assemblages.

The earliest stage in the reaction is to be seen in the development of narrow coronas of amphibole about iron

ores, olivine, and pyroxenes that are adjacent to felspars.<sup>(8) (9)</sup> Gradually the pale green amphibole assumes a brown colour and large irregular crystals of brown hornblende began to surround pyroxenes, etc., and push their way between and envelop crystals of plagioclase. Finally the rock became highly poikilitic and very rich in hornblende, which appears to arise at the expense of all the other minerals, including plagioclase.

Eventually the invading magma consolidated as a basified diorite, so the pyroxene-diorite is thus intimately associated with the more basic types and acts as a kind of cement to the shattered norite mass.

It has been shown in an earlier publication<sup>(11)</sup> that tongues of basified diorite have been injected into the limestones and thereby contaminated. The tongues often contain small recrystallised xenoliths, and it is thus evident that the pyroxene-diorite was actually a magma, but that it contained solid fragments. The tongues probably cooled fairly quickly, and there was not sufficient time for complete assimilation of the xenoliths. In the main mass of basified diorite the smaller basic fragments have lost their identity, and only large scattered masses of the norite remain.

Those portions of the quartz-mica-diorite magma which were not in immediate contact with the roof remained unbasified, and small fragments of the basic hybrids became incorporated as xenoliths without much further hybridisation. The means by which their fine grain size was produced has already been discussed in an earlier publication.<sup>(9)</sup>

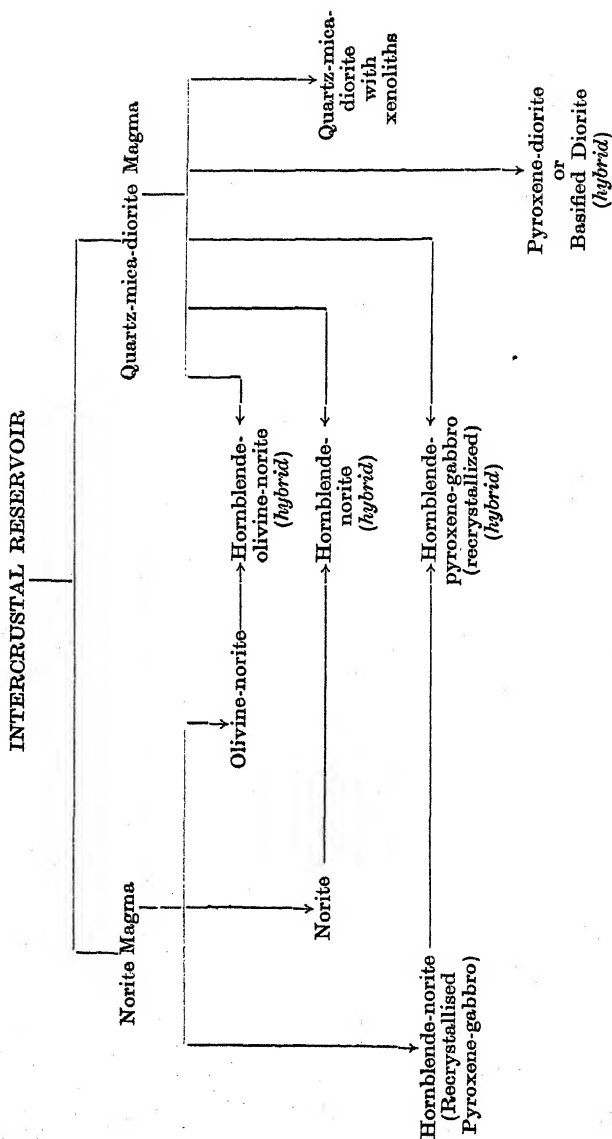
The last phase of igneous activity at Ben Bullen was the injection of veins and small dykes of hornblende-lamprophyre and aplite.

The following diagram is an attempt to show the origin and mutual relations of the various differentiates and hybrids found in the Ben Bullen plutonic complex.

#### Hybridisation and Comparison with Other Areas of Hybrid Rocks.

The writer has already pointed out the significance of hornblende in the formation of the hybrids at Ben Bullen and Hartley,<sup>(9)</sup> and the rocks of these two districts are not only chemically alike but compare as regards order of intrusion and mutual relations of the various differentiated and hybridised types.

DIAGRAM TO SHOW POSSIBLE RELATION OF DIFFERENTIATES AND HYBRIDS.



Olivine has not been found at Hartley, but in this area the most basic rocks have been recrystallised and it is possible that olivine may have occurred in the primary differentiate.

The term "norite" has been applied to certain of the Ben Bullen types, and rocks of the same composition at Hartley have been designated "pyroxene-gabbros". At Ben Bullen the hypersthene appears to be of primary consolidation, and it is fitting that the rocks should be called norites, whilst at Hartley it is uncertain whether the hypersthene is primary or whether it has arisen by recrystallisation of augite and hornblende. The Hartley pyroxene-gabbros may have been norites originally, but owing to this uncertainty it seems better to use the term "norite" only for those rocks which contain definite, primary hypersthene.

The basic complex with its related hybrids at Ben Bullen and the Cox's River intrusion at Hartley have many points in common with noritic hybrids of other areas. A parallelism with certain of the hybrid reactions has already been drawn with the rocks of Trégastel,<sup>(16)</sup> and they may also be compared with types from Loch Doon<sup>(6)</sup> and Cairnsmore of Carsphairn,<sup>(4)</sup> Scotland.

## 5. SUMMARY.

The Ben Bullen complex has been shown to consist of two separate consanguineous intrusions, the earlier and more basic of which has differentiated *in situ*. The later intrusion has reacted with the solid rocks of the first intrusion and a series of cognate hybrids have been formed.

Primary differentiates and hybrids take their places on a variation diagram typical of a calcic series, and certain chemical peculiarities indicate that the Ben Bullen and Hartley complexes are probably co-magmatic. The hybrids and method of hybridisation at Ben Bullen also compares with Hartley.

## 6. ACKNOWLEDGMENTS.

The laboratory work has been carried out in the Department of Mineralogy and Petrology, Cambridge, and the writer wishes to thank Professor C. E. Tilley for kindly reading part of the manuscript of this paper.

For financial assistance she is indebted to the Department of Scientific and Industrial Research, London, to Newnham

College, Cambridge, and to the Australian and New Zealand Association for the Advancement of Science.

She would also like to acknowledge the kindness of Ben Bullen residents, particularly the hospitality of Misses M. and R. Larkin.

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# AN ATTEMPT AT QUANTITATIVE ANALYSIS OF SILVER-GOLD ALLOYS BY OPTICAL SPECTROSCOPY.

By WINIFRED MANKIN, M.Sc.

Communicated by PROFESSOR O. U. VONWILLER.

(*Manuscript received, May 22, 1936. Read, June 3, 1936.*)

Some time ago work was undertaken with the object of ascertaining whether heavy elements could be detected in animal tissue by optical spectroscopy, and a paper was published summarising the results obtained.\* Originally it was hoped to develop spectroscopic methods for the quantitative determination of such elements, but in view of obvious difficulties it was felt that experiments made with less complex material might prove a useful preliminary.

Professor Vonwiller suggested that it might be profitable to examine the spectra of alloys containing metals characterised by a similar arrangement of energy levels, as the relative intensities of corresponding lines might vary in a definite manner with the proportions of the metals. Gold and silver were selected for experiment; with these the arrangements of energy levels are nearly alike, and several pairs of corresponding lines come within the limits of the visible spectrum, so being suitable for the spectral apparatus available at the time.

The pairs of lines selected, in the arc spectra, were :

|                       |             |        |       |      |       |
|-----------------------|-------------|--------|-------|------|-------|
| $^2P_{3/2}-^2S_{1/2}$ | wavelengths | silver | 4669, | gold | 4241. |
| $^2P_{3/2}-^2D_{5/2}$ | "           | "      | 5465, | "    | 4793. |
| $^2P_{3/2}-^2D_{3/2}$ | "           | "      | 5472, | "    | 4811. |

## EXPERIMENTAL METHOD.

A D.C. arc was employed, the alloy forming a bead in a depression in the lower pole, the current flowing between the bead and the upper pole. The voltage was about 250 and the current three ampères. Carbon electrodes were found to be the most suitable of those available. The

\* JOURN. AND PROC. ROYAL SOCIETY OF N.S.W., 1932, 66, p. 509.



upper one was pointed at its lower extremity, and the lower one was tapered and slightly hollowed at its upper extremity. It was found easier to maintain a steady arc by making the lower electrode the negative pole. The alloy was supplied in sheet form. As a preliminary to each exposure a small spherical button of alloy was made by placing a rolled strip of it on the lower pole, completing the circuit by bringing the electrodes into position, then separating them sufficiently to break the circuit after a very small interval of time (at most a very few seconds). The exposure was then made by placing the button on the lower electrode, moving the electrodes into position to complete the circuit and focusing the arc on to the slit of a Hilger spectrometer type D1.

A reducer (blue glass) was placed in a suitable position in front of the spectrometer slit so that each spectrum would show an upper portion of reduced intensity and a lower portion of full intensity. On each plate four photographs of arc spectra were taken, and for calibration purposes a number of continuous spectra obtained from a six volt tungsten lamp (1.75 amps. current for twenty seconds). The intensities of the continuous spectra varied by known amounts corresponding to the slit widths used.

A number of plates were exposed using the above technique. The details of time of exposure and composition of the alloy will be found in the accompanying table.

In view of the great irregularity in the results obtained, no relation being indicated between the relative intensities and the composition of the alloy, it seemed probable that the relative rate of volatilisation of the two metals might have varied considerably in the several experiments, even when the proportions were the same initially, because slight differences in the conditions of the arc might be accompanied by large local differences in temperature. The various beads used had been kept, and accordingly an analysis of these was made by the following method.

#### CHEMICAL ANALYSIS OF ALLOYS.

The remainder of the buttons varied in weight from 0.03 grm. to 3 grms. The button, after being weighed accurately, was dissolved in *aqua regia* in a pyrex vessel on a hot plate. The resulting solution was then evaporated several times with hydrochloric acid in order to remove nitric acid. The whole was next diluted with distilled water, transferred to a centrifuge tube and centrifuged.

The filtrate was carefully removed, leaving the silver chloride in the tube. This procedure was repeated until the precipitate was free from acid and gold chloride. The silver chloride was then dissolved in one-fiftieth normal potassium cyanide and the excess cyanide titrated with one-hundredth normal silver nitrate in the presence of a small amount of potassium iodide.

On estimating silver in materials of known composition it was found that the method was reasonably accurate. For example 0.1105 grm. of an alloy containing 10 per cent. silver and 90 per cent. gold was found on analysis to yield 0.0126 grm. silver. The correct result would have been 0.01105 grm. silver.

#### METHOD OF COMPARING INTENSITIES OF LINES.

From the results obtained by photometry the continuous spectra at the site of each wave-length previously mentioned, curves were plotted showing the relationship of slit width to density at each of the above wave-lengths.

The densities of the lines in the metal spectra at the wave-lengths were obtained by a Moll micro-photometer.\* By means of the density slit width curves the density of any particular line could be expressed as a function of slit width, and therefore ratios of densities of lines have been expressed as ratios of slit width. In some cases it has not been possible to reduce the intensity of lines sufficiently to determine their density by the photometer.

The absolute determination of relative intensity of lines was not made. This would have involved corrections depending on the colour temperature of the standard lamp, and for the variation with wave-length of the dispersion of the prism. Owing to the failure to obtain accordant results this was not justified.

#### SUMMARY AND DISCUSSION.

Buttons of silver gold alloys were placed in the crater of the lower pole of a carbon arc. No definite relations have been found between relative intensity of corresponding lines and composition of the alloy. This seems due mainly to change in composition of alloy during running of the arc, this varying in wide limits in different trials.

---

\* The photometric measurements were made with the aid of a Moll Micro-photometer, portion of the physical equipment purchased by the University from the Cancer Research Fund.

The change in composition appeared to have no direct relation to the time of exposure, but this is only to be expected as one had no knowledge of the actual temperature of the arc. On referring to the ratios of the intensities of corresponding lines the majority of results show that the ratio of silver intensity to gold intensity did increase with increasing percentage of silver. Such was not invariably the case, however, and can be accounted for by considering hypothetical illustrations such as the following:

Suppose that two exposures are made, using in each case a button weighing initially 5 grms. and containing initially 10 per cent. of silver and 90 per cent. of gold. Suppose that the conditions, time, temperature, etc., differ in the two arcs so that at the end one button weighs 2 grms. and the other 4.5 grms., but that each contains 8 per cent. of silver and 92 per cent. of gold. It is readily seen that the first button has lost 0.34 gm. of silver and 2.66 grms. of gold, while the second has lost 0.14 gm. of silver and 0.36 gm. of gold, so that the ratio of the loss of silver to the loss of gold is 1:7.8 in the first and 1:2.6 in the second, although the proportion of silver to gold was the same in each button at the beginning and the same in each at the end. The example is an exaggerated one, but it serves to point out that one might reasonably expect such variations as have appeared in the results. Unfortunately the initial masses of the buttons were not determined, so that it was not possible to examine the results for a possible correction between relative intensities of lines and amounts of metals consumed.

Negative results have shown that technique with buttons would have to be considerably modified; one might obtain more consistent results using rods of alloys, and further improvement might result in the use of spark spectra, which would not result in such rapid consumption of the alloy. Circumstances are such that I have no opportunity at present of carrying out further experiments along suggested lines. The results have been submitted for publication, as it is felt they may have some interest for others engaged in similar work.

#### ACKNOWLEDGMENTS.

The work was done at the suggestion of, and entirely under the direction of, Professor Vonwiller, of the Department of Physics, Sydney University, and I find it difficult to express adequately my thanks to him for all

the help he has given and the apparatus he has put at my disposal during its progress.

I also wish to thank Professor Eastaugh, of the Department of Metallurgy, for supplying the alloys, and Professor Davies, of the Department of Physiology, for enabling me to carry out the chemical analysis.

TABLE OF RESULTS.

| Plate Number | Percentage of Silver Before Exposure in Arc. | Percentage of Silver Found by Analysis After Exposure. | Time of Exposure in Arc and Time Spent in Making Button. | Uncorrected Ratio of Intensity of Lines Expressed as Ratio of Slit Width. Ag: Au. |              |              |
|--------------|--|--|--|---|--------------|--------------|
|              |  |  |  | 4669<br>4241  | 5465<br>4793 | 5472<br>4811 |
| 1a           | 10   | 5.6  | 2 25   |   | 0.96         |              |
| 1b           | 2½   | 2.9  | 40   |   | 0.303        | 2.7          |
| 1c           | 2½   | 3.3  | 1 35   |   | 0.17         | 1.33         |
| 1d           | 10   | 9.9  | 50   |   | 0.2          |              |
| 3a           | 40   | 59.1   | 30   | 1.0   |              |              |
| 3b           | 5  | 5.5  | 25   |   | 2.5          | 2.18         |
| 3c           | 2½   | 2.5  | 45   |   | 1.25         | 1.4          |
| 3d           | 40   | 43.1   | 55   | 1.0   |              |              |
| 4a           | 2½   | 2.9  | 45   |   | 0.86         |              |
| 4b           | 10   | 12.3   | 20   |   | 1.0          |              |
| 4c           | 5  | 7.3  | 35   | 0.43  |              |              |
| 5b           | 2½   | 6.7  | 20   | 1.54  |              | 6.6          |
| 5c           | 5  | 5.6  | 15   |   |              | 5.9          |
| 6b           | 2½   | 2.6  | 27   |   | 0.70         | 1.62         |
| 6c           | 5  | 5.8  | 10   |   | 1.91         | 2.67         |
| 6d           | 40   | 51.7   | 10   | 1.24  |              | 5.4          |
| 7a           | 10   | 13.4   | 15   |   | 3.55         | 1.0          |
| 7b           | 5  | 6.1  | 10   |   | 2.29         | 2.07         |
| 7c           | 2½   | 5.6  | 25   | 0.162   | 2.0          | 3.64         |
| 8c           | 2½   | 12.1   | 50   | 0.455   | 1.20         | 1.67         |
| 8d           | 10   | 12.5   | 30   | 4.73  |              | 2.84         |
| 9a           | 5  | 15.6   | 1 35   | 2.13  |              | 8.0          |
| 9b           | 2½   | 4.2  | 1 35   | 2.51  |              | 4.1          |
| 9d           | 40   |  | 30   |   |              | 17.8         |

# GEOLOGY OF NORTH-WEST BASIN, WESTERN AUSTRALIA, WITH PARTICULAR REFERENCE TO THE STRATIGRAPHY OF THE PERMO-CARBONIFEROUS.

By H. G. RAGGATT, M.Sc.,

*Geological Survey of New South Wales.*

(With Plates III-V and eight text-figures.)

(Manuscript received, April 22, 1936. Read, June 3, 1936.)

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## INTRODUCTION AND ACKNOWLEDGMENTS.

This paper presents some of the results of the author's work in Western Australia during 1934 and 1935, for Oil Search Ltd., under the general direction of the Company's chief geologist, Mr. D. Dale Condit.

Following a short reconnaissance trip by Messrs. Condit and Rudd in 1934,<sup>(12)</sup> the author was in the field for three months, and in 1935 (in company with Dr. K. Washington Gray) for seven weeks.

The area described consists of about 14,400 square miles in the North-West district of Western Australia (see map inset in Plate III). Of this area about 6,000 square miles between the Gascoyne and Lyndon Rivers was examined in some detail.

The paper deals mainly with the stratigraphy and lithology of the Permo-Carboniferous in the North-West Basin, its correlation with that of the Irwin River, and the stratigraphy of the Cretaceous. Tertiary and Post-Tertiary rocks, which occupy a fairly large part of the basin, are referred to only incidentally.

Examination of bore cores, assembly of bore data, and correlation thereof, formed an important part of the investigation, but are referred to only very briefly in this paper.

The author gratefully acknowledges the generosity of the Managing Director of Oil Search Ltd. in giving permission for this paper to be published. Thanks are due specially to Mr. D. Dale Condit for helpful criticism. The author acknowledges indebtedness to Dr. K. Washington Gray for discussion and kindly co-operation in the field; to Mr. F. Chapman and Miss Irene Crespín, Dr. F. W. Whitehouse and Mr. H. O. Fletcher for help in their special branches of palæontology; to Mr. Eric A. Rudd for excerpts from his Wooramel River Report; to Mr. F. Forman for permission to examine files and samples in the office of the Geological Survey of Western Australia, and to other friends and colleagues the nature of whose assistance is specially acknowledged in the appropriate place in the text.

The kindness and willing help of station owners and managers and of the Carnarvon staff of Messrs. Dalgety and Co. Ltd. in furthering the field investigations, and of Messrs. Davis, Hankinson and Co., Perth, in furnishing bore data are also remembered with gratitude.

## PHYSICAL CONDITIONS.

The region described in this paper lies north of the Gascoyne River, west of the 116th east meridian, and is otherwise bounded by the coast between Carnarvon and Onslow. It lies between latitudes  $21^{\circ} 30'$  south and  $25^{\circ}$  south.

Excluding the North-West Cape Peninsula the region may be described topographically as consisting very largely of a plain rising gently from near sea-level at the coast to about 800 feet above sea-level at a distance of sixty to eighty miles inland; it continues to rise to the east. Rising above this plain are a number of flat-topped hills, chief of which are the Kennedy, Moogooloo and Bidgemia (a new name) Ranges. These ranges are the eroded remnants of a surface which also sloped towards the sea. Its seaward outliers (mesas) rise to 500 to 600 feet above sea-level, but the main masses rise to 1,100 to 1,200 feet. Further east the hills rise to greater heights. The Kennedy Range at its widest part has a width of twenty-five miles, but the other ranges are not more than a mile or two in width at the most. (See Figs. 7 and 8.)

From the head of Salt Lake the Cardabia-Giralia Range stretches north almost to the head of Exmouth Gulf. A low scarp forms the eastern side of the range; the western side falls gently towards the sea. Probably at no point does this range exceed 400 feet in height.

In the North-west Cape Peninsula are the Cape and Rough Ranges; these have the rounded profiles of fold ridges. The Cape Range is well defined for about sixty-five miles from Point Cloates to North-west Cape; it occupies almost the whole Peninsula and rises to a height of about 1,200 feet above sea-level. Rough Range is about fifteen miles in length, and at its highest point is about 350 feet above sea-level. Between the North-west Cape Peninsula, Giralia Range and the sea is an interesting area composed very largely of fixed sandhills, which reach a general level of about 150 feet above the sea.

The drainage pattern is simple. The Gascoyne, Minilya and Lyndon Rivers flow parallel to each other over the westward sloping surface, and the Ashburton and Yannarie over the northward. These rivers flow only for short periods in wet seasons. That part of the region north of Winning Pool has an average annual rainfall of 11.67 inches, that south of Winning Pool 9.16 inches. Most of the rain falls between January and July.

Almost the entire region is covered either with low scrub or spinifex. The river banks are lined with eucalypts, but the number of trees away from streams is insignificant. Sandhills, dry sandy stream beds, thickets and deep narrow washouts present obstacles to motor travel, but unless rain falls it is possible to get over a surprisingly large proportion of the region by motor vehicle. As most of the area is occupied for pastoral purposes, its water resources are being gradually exploited, and there are a large number of shallow bores and wells yielding water generally suitable for camp requirements.

The area of rock outcrop is probably considerably less than 50 per cent. of the total, but that part of the area in which there are few or no outcrops happens to have been most intensively prospected for water by boring, and the main geological boundaries can thus be deduced with sufficient accuracy to give a fairly good regional picture of the geology. There are good exposures of the Tertiary, uppermost Cretaceous, basal Cretaceous, and a considerable part of the Permo-Carboniferous, particularly the Kennedy sandstone, Wooramel sandstone, Callytharra limestone, and upper part of the Lyons Series. The remaining Permo-Carboniferous units are sufficiently well exposed for stratigraphical measurements in places, but structural work would be difficult in some areas.

#### PREVIOUS WORK.

The earliest work was that of J. W. and F. T. Gregory,<sup>(1) (2)</sup> who gave a picture of the general succession and structure of the region which is strikingly near the truth. Sir John Forrest's palæontological collections from the Gascoyne almost to the Minilya added materially to knowledge of the Permo-Carboniferous of that area.<sup>(3)</sup> A. Gibb Maitland described part of the Permo-Carboniferous sequence in general terms.<sup>(4) (5) (6)</sup> He demonstrated the presence of glacial beds in the lower part of the sequence, which he named the "Lyons Conglomerate".<sup>(4)</sup> He was the first to recognise the artesian water possibilities of the region.

F. G. Clapp has published three papers, one<sup>(7)</sup> giving general observations, and two<sup>(8) (9)</sup> dealing mainly with oil possibilities. Clapp's most noteworthy contribution to the geology of the region was the discovery of folded Tertiary strata on North-west Cape.



W. G. Woolnough (<sup>(10)</sup>, pp. 52-53), during an air reconnaissance in 1922, noted folding and faulting in the Permo-Carboniferous along the Gascoyne River, and verified the anticlinal structure of the Cape Range and other coastal hills southwards to Salt Lake.

E. A. Rudd and T. W. H. Dee, in a report based on work done for Oil Search Ltd. in 1932,<sup>(11)</sup> were the first to define stratigraphic units of the Permo-Carboniferous other than the "Lyons Conglomerate" of Maitland. The value of their work is stressed in the following pages.

In a recent paper D. Dale Condit<sup>(12)</sup> gave a brief résumé of the results of field work done by geologists of Oil Search Ltd., and a discussion of the significance of the results as bearing on oil possibilities.

A comparison of the geological maps accompanying the present paper with the latest published maps will show that little was really known about the distribution of the various systems represented in the area. The whole of the area formerly shown as Jurassic is Cretaceous, as also is much of that shown as Permo-Carboniferous. The thickness and distribution of the subdivisions of the Permo-Carboniferous were also almost unknown.

#### STRATIGRAPHY.

The table on p. 105 summarises the stratigraphical succession of the region.

No igneous rocks (except those of the basement complex) have been reported by any geologist who has visited this region. The geological map (Plate III) shows the distribution of the systems. It is based largely on original observations, but includes notes made by Condit and Rudd and by Washington Gray. The boundary of the Pre-Cambrian is taken in part from the map of Western Australia issued by the State Geological Survey in 1933.

As this paper deals mainly with Permo-Carboniferous stratigraphy, the other systems are described only very briefly.

#### Pre-Cambrian.

The basin of late Palæozoic to recent sediments is bounded on the east by a complex of schist and granite. All the outcrops of Pre-Cambrian observed between the Wooramel and Arthur Rivers consist of granitised schist.

Between Mt. Sandiman and Wogla Station on the Yannarie River (and including the head of the Lyndon)

## Summarised Statement of Stratigraphical Succession.

|                            |  | Thickness<br>in Feet.            |   |
|----------------------------|--|----------------------------------|---|
| Post-Tertiary.             |  |                                  | Shelly sands; oolitic limestones and travertinised sands; dune sands.   |
| Tertiary.                  | Mio-Pliocene.                              | Unconformity.                    | White coralline and foraminiferal limestone and hard travertinised sands.   |
|                            | Miocene ?                                  | 100 +                            | Well bedded white foraminiferal limestone.  |
|                            | Lower Miocene                              | } 600 +                          | White, pink and yellow <i>Lepidocyclina</i> limestones.<br>Detrital limestone with <i>Discocyclina</i> and nummulites.  |
|                            | — Upper Oligocene ? Eocene.                |                                  |   |
| Cretaceous.                | Cardabia Series.<br>(Campanian-Thuronian). | Disconformity.<br>855-1,050.     | Mainly chalks and marls; polyzoal limestones and glauconite sand with ammonites in upper portion (Campanian).   |
|                            | Winning Series<br>(Albian).                | 100-1,240.                       | White and vari-coloured silts, radiolarian cherts and glauconitic sandstones.   |
| Permian-<br>Carboniferous. | Gascoyne Series.                           | Unconformity.<br>4,250-5,000.    | Limestones, sandstones and shales divided into following stages:<br>Wandagee. Shale, argillaceous sandstone and sandy limestone. Marine. Thickness, 1,250-1,450 feet.<br>Kennedy. Sandstone, marine. Thickness, 400-700 feet.<br>Byro. Mainly marine argillaceous sandstone and sandy shales in upper half. Thin-bedded sandstones (marine) and sandy to carbonaceous shales in lower half (mainly marine, but freshwater in part). Small erratics towards base. Thickness, 2,300 feet. |
|                            |  | Disconformity ?                  | Wooramel. Sandstones with some thin quartz pebble bands. Sparse marine fauna. Thickness, 130-280 feet.<br>Callytharra. Flaggy limestones and calcareous shaly mudstones. Richly fossiliferous: marine. Thickness, 200-400 feet.   |
|                            | Lyons Series.                              | Disconformity ?<br>2,150-2,400 + | Upper 300 feet mainly shales, with sandstones and limestones. Remainder fine grained sandstone with glacial boulder beds and some shales. Glacial erratics up to 12 feet in length. Marine fossils at intervals.  |
| Pre-Cambrian.              | Mosquito Series.                           | Unconformity.<br>—               | Schists and phyllites intruded by granite.  |

the principal rock is a coarse-grained red granite of normal type. At Wogla this is seen to intrude schists, highly folded, but with a dominant strike north  $70^{\circ}$  west. This type of granite occurs also on the Ashburton at Peepingee Pool.

Downstream from Wogla to Barradale Pool, below which the outcrops are obscured by recent deposits, the Pre-Cambrian consists of silky and quartz schists striking as above mentioned. This association seems to be typical of the Mosquito Series of Western Australia.<sup>(13)</sup>

### Permo-Carboniferous.

#### Introduction.

Overlying the Mosquito Series and underlying the Cretaceous is a considerable thickness of sediments, dominantly marine. Throughout the sequence there is no marked break, either faunal or tectonic. Except for the evidence of glacial conditions in the lower part, the record is one of more or less continuous deposition under oscillating conditions, similar lithological types appearing more than once in the sequence.

Palæontological investigations are incomplete, but some tentative remarks on the faunas are offered.

Although in terms of European time equivalents there is no marked faunal break, there are differences in the faunal content. Forms such as *Dibunophyllum*, *Ætomaccladia ambrosoides* and *Rhombopora tenuis*, which are typical Upper Carboniferous forms, are restricted to the Lyons and Callytharra Stages, and *Orthis* (*Rhipidomella*) cf. *australis*, which is found in the Burindi Series (Lower Carboniferous) of New South Wales, occurs only in the Lyons. Other Carboniferous fossils such as *Cleiothyridina macleayana*, *Spirifer byroensis*, *Chonetes hardrensis*, *Productus semireticulatus* and *Plerophyllum australe* are, however, found in the Byro (some of them high up in that stage), whilst *Chonetes pratti* occurs in the Byro and Wandagee beds.

Of fossils characteristically Permian, *Chonetes hardrensis* var. *cracowensis* and *Tribrachiocrinus* sp. are confined to the Byro, whilst *Cardiomorpha blatchfordi*, *Aviculopecten*, *Spirifer musakheylensis* and *Strophalosia clarkei* are not found below the Wooramel sandstone. *Deltopecten subquiquelineatus* (*comptus*) common in the Upper Marine of New South Wales (Permian) is known only from the

middle of the Byro, and *Spirifer rostralinus* var. *crassus* only from the Wandagee beds. *Linoproductus cancriniformis*, which is not found below the Permian in Europe and India, occurs in the same beds as *Deltopecten subquiquelineatus*.

The writer considers that the Olive Shales of the Irwin River, with their well known cephalopod beds, may be correlated with the shales forming the upper part of the Lyons Series (see discussion, pp. 64-68). The latest identification of this cephalopod as *Metalegoceras Jacksoni* (see <sup>(14)</sup>, *addenda et corrigenda*) gives a distinctly Permian aspect to the whole sequence above the main glacial beds.

Summarising, it will be noted that Permian forms occur down to the base of the Wooramel Stage at least. The faunal aspect of the Lyons Series is Carboniferous; some forms, which elsewhere occur in the Carboniferous, range well up in the sequence.

In 1932 (<sup>(14)</sup>, footnote, p. 61) Sir Edgeworth David proposed the term Kamilaroi for "the sequence of rocks in Australia and Tasmania characterised throughout by a *Glossopteris-Gangamopteris* flora and by a fauna which, while distinctly Permian above and with Upper Carboniferous affinities below, is nevertheless linked together by a number of characteristic common forms such as *Trachypora wilkinsoni*, *Eurydesma hobartense*, etc."

Definition of the upper limits of the Kamilaroi presents no great difficulty in New South Wales, but in the absence of freshwater beds in the upper part of the Permo-Carboniferous sequence, and of the lower Mesozoic in North-Western Australia there is a little difficulty even here. But the real difficulty (as Sir Edgeworth David was fully aware) lies in defining a lower limit. To refer to the Western Australian sequence as Kamilaroi implies a correlation of the Lyons glacials with those of the Lower Marine in New South Wales, and it is at least doubtful if this can be sustained.

From this brief discussion it is clear that "Permo-Carboniferous" is the only satisfactory term to apply to the sequence in the North-west basin of Western Australia, and that the use of "Kamilaroi", at present, is inadvisable.

#### General Relationships.

The area of outcropping Permo-Carboniferous in the North-west Division is now fairly definitely known. From

the Gascoyne northwards the Permo-Carboniferous occupies an area of about 5,000 square miles. The observations made on the Yannarie and Ashburton Rivers, where the Cretaceous beds rest upon the basement schists, show the limit of outcrop of the Permo-Carboniferous in that direction, and the Onslow bore (No. 1,\* depth 1,728 feet) does not appear to have entered rocks of this system. The bore data furnish evidence of the extension of Permo-Carboniferous beds beneath a cover of younger sediments both beneath the coastal plain on the lower Wooramel, Gascoyne, Minilya and Lyndon Rivers and north-westerly for forty miles from the northernmost outcrops on Mia Mia Station to Cardabia.

The Permo-Carboniferous rest with marked unconformity upon the Pre-Cambrian, and are overlain wherever observed in the North-west by marine rocks of Cretaceous age.

The contact of the Permo-Carboniferous and Cretaceous is rarely seen, but it is a general experience to find Permo-Carboniferous beds dipping at angles up to  $22^{\circ}$  and the Cretaceous nearby with no appreciable dip. In general the difference in dip in exposures a few miles apart is about  $10^{\circ}$ .

Proof of the fact that these differences in dip are an expression of unconformity in some places is provided by a section at the foot of the breakaways east of the 109 mile post in the rabbit-proof fence which forms the western boundary of Lyndon Station.

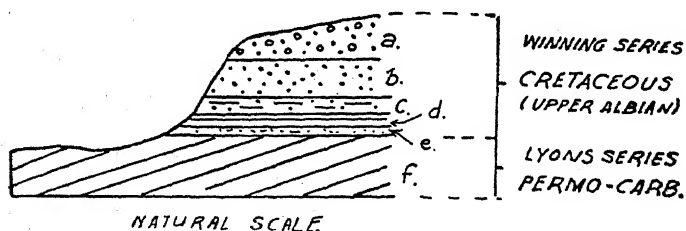


Fig. 1 (a).—Unconformity between Cretaceous and Permo-Carboniferous, eight miles north-north-east from K.52.

- a 4 ft. White micaceous sandstone with white quartz pebbles.
- b 20 ft. Coarse gritty green sandstone.
- c 6 ft. Ferruginous argillaceous sandstone.
- d 2 ft. Yellow shale.
- e 6 ft. White siltstone.
- f — Grey shale with highly ferruginous concretionary bands and some pebbles and boulders.

\* Numbers of bores refer to maps and list on pp. 171-172.

Along the western face of the Kennedy Range three to four miles South of the 70 mile post in the rabbit-proof fence (ten miles south-west of K.54) the following section is exposed :

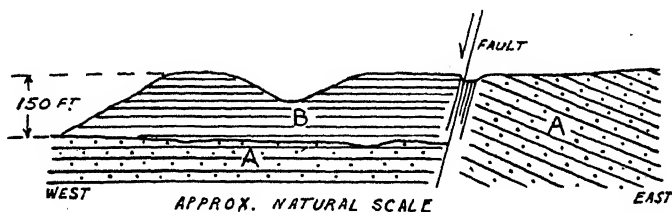


Fig. 1 (b).—Faulted contact between Cretaceous and Permo-Carboniferous, Middalya Station, ten miles south-west from K.54.

A. Kennedy sandstone, Permo-Carboniferous.

B. White and yellow sandy silts and cherts. Upper Albian.

The fault zone is marked by a highly ferruginous cavernous sandstone. It dips south-west at about  $75^\circ$ , and apparently extends to the south for a long distance, generally similar relationships having been noted fifty miles south of this point. The amount of throw is unknown, but is at least 150 feet. It will be seen from the section that the Cretaceous beds on the downthrow side of the fault rest upon almost undisturbed Kennedy sandstone, the Wandagee beds being absent. The section suggests that the Cretaceous was deposited upon a broad arch in the Permo-Carboniferous, after erosion of the Wandagee beds; faulting and erosion followed.

Sections based on a study of the logs of the large number of bores which have been put down in the deeper part of the basin suggest that the relationship here is that the Permo-Carboniferous was folded into broad structures, the anticlines suffering denudation in general down to the top of the Kennedy sandstone. The Cretaceous was then deposited on a rather uniform base, and both were subsequently folded, the old warps controlling the locus of the new ones. There appears to be but slight angular discordance between the beds of the two systems in the deeper parts of the basin.

In the Irwin River Valley, as is well known, freshwater Jurassic rocks rest upon the Permo-Carboniferous.

### Summary of Stratigraphy.

The stratigraphic column as now worked out for the Permo-Carboniferous in the North-west Division, arranged in descending stratigraphical order, may be summarised as follows :

*Gascoyne Series.* Shales, sandstones, sandy mudstones and limestones divided into the following stages :

**Wandagee Stage.** Very largely shale, as much as 500 feet being present as one unit at type locality ; thin bedded friable sandstone and sandy limestone. Principal fossils : *Aulosteges ingens*, *Spirifer rosalinus* var. *crassus*, *S. marcoui*, *S. convolutus* and *Chonetes pratti*, which are abundant on restricted horizons. Thickness, 1,250 to 1,450 feet.

**Kennedy Stage.** Almost wholly sandstone, including dense blocky ferruginous, well bedded white micaceous, and fine grained yellowish brown types. Ferruginous fossil casts and concretions found in some places, *Strophalosia clarkei* perhaps commonest fossil. Other fossils include *Spirifer byroensis*, *Spirifer musakheylensis*, *Cardiomorpha blatchfordi*. Maximum known thickness, 700 feet.

**Byro Stage.** Sequence exposed on Gascoyne River : (a) Carbonaceous shale at base overlain in turn by (b) sandy limestone, calcareous sandstone and dark shales, with a few small glacial erratics ; (c) sandy mudstones, dark shales, and soft white sandstone ; (d) thin cross-bedded brown to greenish brown sandstone with abundant small spherical concretions and abundant *Deltopecten* aff. *subquiquelineatus* and *Tribrachiocrinus* sp. ; (e) massive sandy micaceous mudstone with large calcareous lenses and dark to sandy shales. *Spirifer byroensis* plentiful.

The sandy mudstones (e) persist to the Minilya River, but the remainder pass almost entirely into dark to carbonaceous and sandy shales ; still further north bore provings suggest that the whole stage is shaly, with some calcareous beds.

In addition to the *Deltopecten*, the commonest fossils are *Chonetes hardrensis* and *C. pratti*.

Carbonaceous matter and probable plant remains are found in dark shales interbedded with marine strata. Thickness, not less than 2,400 feet.

Wooramel Stage. Mainly medium grained white micaceous sandstone, cross-bedded at top in places. Shaly sandstone in lower portion in some northern sections. A very few poorly preserved marine fossils. Thickness, 130 to 280 feet.

Callytharra Stage. Commonly divisible into an upper flaggy limestone and a lower calcareous shaly mudstone with thin, hard, limestone bands. Rich and varied marine fossil content including *Plerophyllum*, *Monilopora*, *Dibunophyllum*, *Phialocrinus*, *Evactinopora*, *Syringothyris*, *Seminula*, *Cleiothyridina*, *Modiolus* and *Warthia*. *Fenestellidæ* abundant in shaly beds. Thickness, 200 feet in south to 460 feet in the north.

#### *Lyons Series.*

Divisible into two unequal portions on the Gascoyne: an upper shaly group with thin fossiliferous limestone beds and glacial erratics, and a lower more sandy group with not less than eight distinct glacial conglomerates, with abundant erratics and striated pebbles. Becomes more shaly to north. Marine fossils found at intervals, including *Fenestella propinqua*, *Conularia warthi*, *Plerophyllum australe* and *Orthis (Rhipidomella) cf. australis*. Thickness, 2,150 to 2,400 feet.

There is possibly disconformity between the Wooramel and Byro Stages and between the Lyons and Callytharra; otherwise the units are conformable.

The total thickness of Permo-Carboniferous sediments measured on the Gascoyne River and tributaries is about 6,750 feet. On the Lyndon the thickness (including bore data) is 7,350 feet, and if the maximum thicknesses recorded for each unit be added together a figure in excess of 8,000 feet is obtained. Composite comparative columnar sections of the Permo-Carboniferous are given in Fig. 2. Plate IV shows the distribution of the series and stages within the area occupied by the Permo-Carboniferous in the North-west basin.





### Subdivisional Terms.

It will be observed that the sequence, viewed broadly, falls naturally into two divisions, the lower, glacial beds, and the remainder of the column, consisting of shales, sandstones and limestones. As these are the major subdivisions of a system they are termed series, the glacials the Lyons Series, and the remainder the Gascoyne Series.

The Gascoyne Series is further divisible into units, largely, but not entirely, lithological. Thus the Callytharra limestone, Wooramel and Kennedy sandstones are mainly lithologic units; the Byro and Wandagee beds are not, but they consist of alternations of strata which may be grouped together. These are important sequences, subdivisions of a series, and as such may be described as stages.

### Detailed Descriptions of Series and Stages.

Unless there is a statement to the contrary all the sections described and figured in this paper are based on measurements by the writer. Most of these measurements consist of traverses of profiles by tape, pacing (calibrated by reference to survey points), compass and aneroid barometer.

In view of the facts that several of these traverses are some miles in length, the dips fairly low and the topographic relief small, the measurements are best expressed as columns. For instance, the traverse on which the section of the Lyons Series on the Wyndham River is based is eleven miles in length, and the Byro section on the Gascoyne is derived from plotting a pace traverse (checked as stated above) of the banks of the Gascoyne from L.9 to the mouth of the Wyndham (twenty-five miles), and thence up the Wyndham and Arthur Rivers, a further seven miles.

#### (i) Lyons Series.

##### *Definition and General Relationships.*

A. Gibb Maitland<sup>(4)</sup> proposed the name Lyons Conglomerate for a glacial boulder bed which he noted on the Wyndham River and correlated with other occurrences on the Arthur, Lyons, Minilya and Lyndon Rivers. Boulder beds on the Minilya and Lyndon Rivers were referred to as "Lyons Conglomerate" by F. G. Clapp<sup>(7)</sup> in 1925. E. A. Rudd<sup>(11)</sup> noted a boulder bed in the Wooramel area which  
J—June 3, 1936.

he considered could be correlated with that of the type locality.

In the Wyndham River section of the Lyons Series it is shown (pp. 117-119) that there are at least eight distinct glacial boulder beds closely resembling that discovered by Maitland. No doubt due to their lithological similarity and the commonly prevailing low dip, the lower horizons have been confused with that of the original "Lyons Conglomerate". It is also certain that the outcrops at Tchugareywurdoos Pool (two and a half miles east of Gnarree Pool) on Kialawibri Creek, a tributary of the Lyndon, which have been referred to the "Lyons Conglomerate", are not less than 2,000 feet below the horizon known by that name on the Wyndham. Whether or not any one of these horizons is persistent from place to place can be proved only by mapping.

The Lyons Series is defined as including all the Permo-Carboniferous beds below the base of the Callytharra Stage. The Series consists of more than 2,000 feet of strata, most of which show evidence of having been deposited under glacial conditions.

The basal beds of the Lyons Series rest with marked angular unconformity upon a basement composed of granite and schist which are referred to the Mosquito Series. In some places, notably the Arthur River, the basal Permo-Carboniferous merge into featureless plains upon which it is impossible to define accurately the contact between them and the basement rocks.

Faulting at this contact is recorded by Gibb Maitland.<sup>(3)</sup> Maitland states that this faulting may be seen near K.34, at the head of the Davis River (<sup>(6)</sup>, p. 35). This is perhaps a misprint for K.41. The former locality was visited and the rocks were found to be gently dipping Callytharra-Wooramel. K.41 is twelve and a half miles north-east from K.34, and appears to be the nearest Trig Station to the head of the Davis River. The faulting described by Maitland is high angle faulting involving Permo-Carboniferous beds, and is probably late Palæozoic.

E. A. Rudd<sup>(11)</sup> states that the Lyons and Callytharra are conformable in the Wooramel area. In the North-west Basin the relationship between the Upper Lyons and the Callytharra is not known with precision because of the soft nature of the beds, but the marked parallelism in strike and general similarity of dip shows that there is no marked unconformity. What appear in places to be marked

unconformities are local glacial phenomena (see p. 119 and Plate 5, Fig. 1).

There is considerable variation in the lithology of the 300 feet of strata immediately beneath the Callytharra. Illustrations of this are the absence of the limestone conglomerate of the Wyndham River section from that of the Arthur River, and the greater proportion of shale in the Arthur River section as compared with that measured three miles north of the river (see Fig. 3). If followed along the strike, the Callytharra limestone will be found to rest on different lithological types in the Lyons, such as conglomerate, sandstone and shale.

#### *Distribution and Type of Outcrop.*

Northwards from the Wooramel River boulder beds may be seen at intervals to the Gascoyne. Rocks of the Lyons Series were examined on the Wyndham and Arthur Rivers. On the Wyndham these beds occupy a belt ten miles in width in the central portion of Bidgemia Station. Further north this belt, due to folding and preservation from erosion of some of the overlying beds, is split into two parallel belts, trending north-west. The western strip forms part of a denuded anticline, and is five miles wide; the eastern is about seven miles wide. These two belts appear to preserve their identity at least as far as Mt. Sandiman, forty-five miles north from the Arthur River. Their outcrop can be traced without interruption to the Minilya River (both branches), and thence in a well defined belt from three to ten miles in width to the Lyndon River. That is, the Lyons beds outcrop continuously from the Wyndham to the Lyndon, a distance of 130 miles.

Folding and faulting on Williambury Station have led to exposure of Lyons beds as inliers among the younger Permo-Carboniferous formations, and small patches of boulder beds are exposed on denuded folds in the vicinity of Pleiades outcamp on Mia Mia Station. On the Gascoyne River near K.39 is a small faulted block which includes about 1,500 feet of strata apparently belonging to the Lyons Series.

In general, and particularly on the Gascoyne and its tributaries, denudation of the Lyons beds produces boulder-strewn flat country with a few low mesas, the latter largely sandstone. The country occupied by them carries little vegetation, the quartz pebble beds being particularly sparsely covered. As a consequence of this weathering

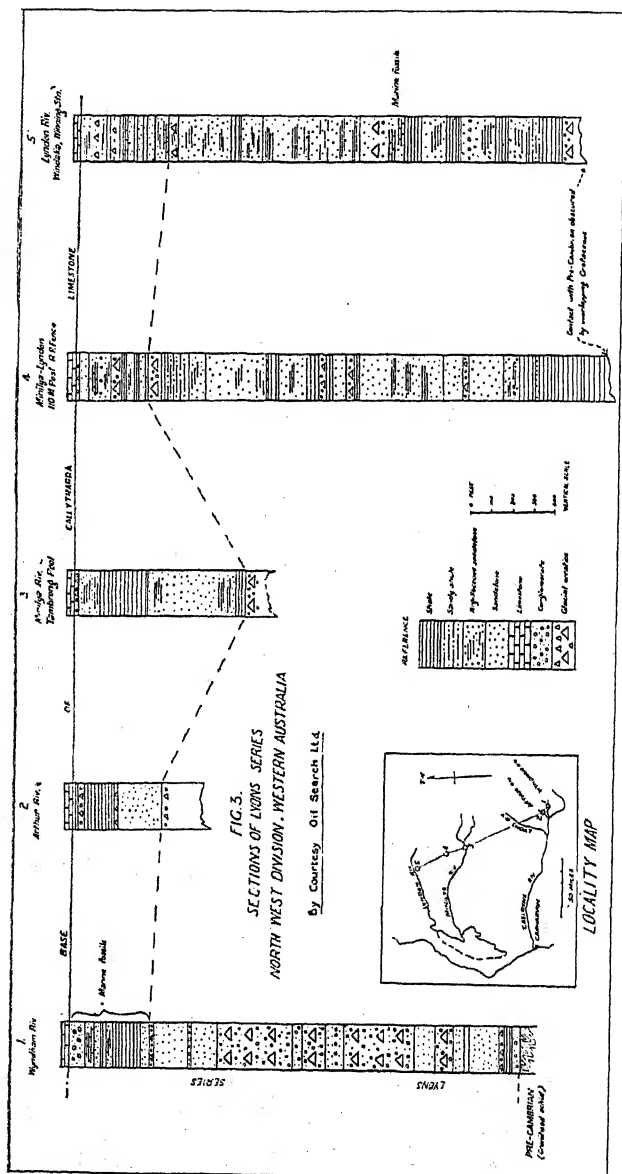


Fig. 3.—Comparative sections of Lyons Series.

the outcrops appear to be mainly boulder beds, and even with the greatest care the amount of other sediments is probably underestimated.

The Callytharra limestone usually forms strike ridges. Where these are breached by streams there are usually good exposures of the upper 300 to 400 feet of strata forming the upper part of the Lyons Series immediately upstream from the gaps. Away from stream sections outcrops of shales may usually be detected by the presence of gypsum in the soil.

### *Lithology and Thickness.*

The Lyons Series consists of sandstone, glacial boulder beds, conglomerate and shale, with a thickness of 2,000 to 2,400 feet.

A complete section is exposed in the valley of the Wyndham, apparently free from duplication or deletion by folding or faulting, as follows :

#### *Section of Lyons Series on Wyndham River.*

##### *Callytharra Limestone.*

380 *Clay shale, fine-grained sandstone and calcareous conglomerate.* A few glacial erratics towards the top. Marine fossils.

20 *Boulder Bed* (original Lyons Conglomerate of A. Gibb Maitland).

160 *Mainly sandstone.*

15 *Boulder Bed.*

125 *White micaceous sandstone.*

350 *Boulder Bed.* Shaly matrix. Granite and silicified limestone erratics common. Group of granite boulders noted with an individual seven feet by four feet.

50 *Mainly white micaceous sandstone* with some boulders up to twelve inches.

110 *Boulder Bed.* Calcareous sandstone lenses one to two feet in length, at base.

90 *Sandstone* with thin beds of pebbles.

325 *White quartz pebble conglomerate* with boulders.

100 *Sandstone.*

85 *White quartz pebble conglomerate* with boulders.

50 *Felspathic (?) sandstone* with a few quartz pebbles.

25 *White quartz pebble conglomerate.* (Pebbles pigeon's egg to four inches in diameter).

- 140 Medium-grained white micaceous *sandstone*.  
20 *Boulder Bed*. Sandy matrix. Largest boulder of granite, four feet by three feet by two feet.  
40 *Shale*. Grey and dense with calcareous concretions.  
40 *Coarse grit to boulder bed*. Varies from coarse felspathic grit with quartz and a few granite pebbles to a bed with boulders commonly one to two feet and up to four feet in diameter.  
— Granitised schist (basement and complex).

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2,165

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The basal bed was found to vary considerably within short distances from a micaceous felspathic grit to a coarse conglomerate, and it is probable that in some places there is an appreciable thickness of strata stratigraphically lower than this bed, the traverse having commenced on a promontory on the Permo-Carboniferous-Pre-Cambrian boundary, and not in a bay.

This section shows the Lyons to consist of two unequal portions, the lower (1,750 feet) consisting of sandstone, boulder beds, and some shale, the upper (380 feet) largely of shale with sandstone, limestone, and a boulder bed. The upper beds contain *Callytharra* type fossiliferous marine limestones and show transition from the lower beds to the *Callytharra* Stage.

It will be noted that the section includes about 720 feet of sandstone. The upper sandstone members are fine grained, and somewhat argillaceous; the lower are medium to fine grained, white and kaolinic. They look chalky, but do not effervesce with cold hydrochloric acid. White mica occurs abundantly in these lower sandstones, some of the pieces being 0.3 inch in diameter.

G. D. Osborne, who has kindly examined a specimen of one of these sandstones, states:

“Under the microscope the rock is seen to be of very fine and even grain. The fragments are mostly of angular quartz, which is clear and unstrained, and appears not to have suffered much transport. For this reason the rock does not appear to be an ordinary sandstone. In addition to quartz there are several pieces of microcline, some albite, occasional wisps of ragged muscovite, and partially chloritised biotite; the matrix is kaolin.”

The specimen described came from a mesa resting almost directly on the granite basement, and the petrological description is in harmony with the view that the rock represents the re-cemented granite detritus of the basement, the cement probably being largely derived from settling out of kaolin from milky waters, released in periods of thaw.

Eight distinct boulder beds are shown in this section. Granite and related rock types predominate amongst the erratics, but silicified limestone and slaty rocks also occur. The fluvio-glacial origin of these deposits is shown by several features, some of which have been described in detail by Maitland,<sup>(4)</sup> and need not be re-described here. Among these are their unsorted lithology, the size of the boulders (up to twenty-five tons), the fact that the large boulders occur in groups rather than uniformly, facetting and scoring of pebbles. The smaller pebbles are well rounded, the larger commonly sharply angular. Probably the fact that numerous large and small, rounded and angular erratics are found in a shaly matrix is as convincing an argument for their glacial origin as any, since there is little likelihood of their getting into an offshore deposit in any other way.

Marked distortion of the bedding planes of a sandstone underlying one of these boulder beds is shown in the bed of the Wyndham. (Plate V, Fig. 1.) This distortion is limited to a depth of ten to fifteen feet below the boulders, and is clearly due to the pushing action of the grounding ice rafts which deposited the boulders. It appears to be a fairly common phenomenon in the upper part of the Lyons Series. A particularly good example may be seen in the bed of the Arthur River, two miles south-west from K.35, where a bar of sandstone in the Lyons Series is exposed, three chains in length and fifty feet wide. It dips almost vertically, and is overlain by Callytharra limestone dipping at two or three degrees. Normal relationships between the beds may be seen a few chains upstream.

White quartz pebble conglomerate is the characteristic matrix of the lower boulder beds. Weathering of these produces the "natural macadam" surfaces referred to by A. Gibb Maitland.<sup>(5)</sup>

The upper 500 feet, including the topmost shaly portion of the series, were measured in greater detail in the Wyndham and Arthur River Valleys (Fig. 3). Towards the



top in the Arthur River a boulder bed with a calcareous shaly matrix occurs, in which a granite erratic, twelve feet in length, was observed. The shales underlying this bed show seasonal banding suggestive of varves, and exhibit perfect cone-in-cone structure.

A section (Fig. 3) of the upper shaly portion of the Lyons Series was measured near Tambrong Pool on the Minilya River. This section shows a boulder bed immediately underlying the shaly Callytharra limestone and underlain in turn by 780 feet of argillaceous sandstone, calcareous grit and shale. These beds overlie a very prominent boulder bed with a conglomerate matrix in which the pebbles are commonly one and a half inches in diameter. A granite erratic, the weight of which is not less than twenty-five tons, outcrops adjacent to the point where the Moogooree-Williambury Road crosses the Lyndon River.

Between the Minilya and Lyndon Rivers there are good sections of the lower Permo-Carboniferous including the Lyons. Towards the Minilya, however, this section is confused by folding and faulting. These folds and faults are less in evidence towards the Lyndon, but the lowest beds are here obscured both by overlapping Cretaceous and by sand dunes.

A partial section was measured near the 110 mile post on the rabbit-proof fence (partly on Lyndon Station and partly on E. Lamont's lease 3627/96 between Mia Mia and Middalya Stations). (Map reference, nine and a half miles north-north-east of K.55.)

*Partial Section Lyons Series 9½ miles N.N.E. of K.55.*

*Descending Order.*

- Callytharra limestone.
- 0 to 5 Conglomerate. Boulders about ten to twelve inches in diameter.
- 150 Mainly argillaceous sandstone with some conglomerate. White sugary sandstone at top.
- 50 Conglomerate with boulders; calcareous lenses.
- 120 Argillaceous sandstone and shale; poor outcrop.
- 60 Boulder Bed; boulders up to four feet.
- 130+ Largely sandy shale with ferruginous bands.
- 75 Thin bedded yellow argillaceous sandstone and sandy shale with ferruginous bands.
- 290 Argillaceous sandstone, white towards top.

- 5 *Boulder Bed.*
- 180 Argillaceous sandstone and shale; upper portion mainly shale.
- 45 *Shale.*
- 40 White quartz conglomerate with erratics.
- 35 *Shale.*
- 65 Ferruginous sandstone.
- 40 *Boulder Bed.* Boulders up to twelve inches.
- 20 Greyish green shale.
- 395 Argillaceous sandstone and sandy shale. Poor outcrop.
- 90 White felspathic (?) sandstone.
- 25 White quartz pebble conglomerate with boulders.
- 160 White micaceous sandstone.
- 75 Argillaceous sandstone with ferruginous sandstone and boulders.
- 390 Mainly grey shale with highly ferruginous concretionary bands and some pebbles and boulders.
- Still lower beds overlapped by Cretaceous.

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2,445

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The comparative columns (Fig. 3) bring out the differences between this section and that of the Wyndham. The principal points are the relative unimportance of boulder beds as compared with the Wyndham, and the more shaly nature of the section generally. The change in lithology of the sandstones from a felspathic to an argillaceous type from the bottom of the section upwards is present here as already described for the Wyndham.

On the Lyndon River the Lyons beds outcrop from near the junction of the river and Kialawibri Creek upstream at least as far as Windalia Pool. The following partial section was measured in this locality :

*Partial section, Lyons Series, Lyndon River.*

- Base of Callytharra.
- 120 Argillaceous sandstone, calcareous grit, boulders and erratics.
- 100 Shale with erratics and lenses of calcareous grit.
- 125 Shale and argillaceous sandstone.

- 105 Shale and argillaceous sandstone with calcareous conglomerate and sandstone. Some large erratics in bottom thirty-five feet.
- 250 Argillaceous sandstone with concretions.
- 50 Mainly shale.
- 95 Argillaceous sandstone.
- 450 Shale and argillaceous sandstone.
- 210 Fossiliferous limestone-conglomerate, ripple marked sandy limestone and hard fossiliferous limestone.
- 735 Argillaceous sandstone and hard cherty shales with dendrites.
- Boulder Bed (Tchugareyurdoo Pool) (two and a half miles east from Gnarrea Pool).

## 2,245

The lowest beds in the above section outcrop at some distance from the known basement rocks, but the structure in the interval between is not known, as the outcrops are obscured by Cretaceous rocks and a heavy mantle of clayey soil in which gypsum crystals occur in great numbers.

### *Palaeontological Notes.*

These notes and those given at the end of the description of each stage of the Permo-Carboniferous are intended primarily to present determinations by F. Chapman and Irene Crespin of fossils collected during the recent work. Some determinations by H. O. Fletcher\* are also included. The notes are supplemented by additional information from previous papers, but do not pretend to be complete. It is possible to refer some of the fossils in earlier lists to the stratigraphical units as now defined, but there is difficulty in using many of the older determinations because the localities from which the specimens were obtained are not always recorded with sufficient accuracy.

A list of the fossils found immediately above and immediately below the top glacial boulder bed on the Wyndham River is given by Maitland <sup>(6)</sup>, p. 35). (For palaeontological descriptions, see Etheridge's paper <sup>(15)</sup>.) *Ariculopecten tenuicollis*, Dana; *Hexagonella dendroidea*, Hudleston; *Pterophyllum australe*, Hinde; *Spirifer musakheylensis*, Davidson; *Spirifer hardmani*, Foord;

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\* Descriptions will appear shortly in *Records Austr. Museum.*

*Spirifer lata*, McCoy; *Reticularia lineata*, Martin; *Cleiothyris* (*Athyris*) *macleayana*, Eth. Fil.; *Chonetes pratti*, Davidson; *Productus* cf. *longistriatus*, Foord; as well as many fragments of crinoid stems and Bryozoa.

He also gives the following as occurring in a limestone conglomerate at K.51, Minilya River: *Amplexus pustulosus*, Hudleston; *Plerophyllum australe*, Hinde; *Productus semireticulatus*, Martin.

Amongst fossils collected by the writer from horizons in the Lyons Series on the Lyndon River, Chapman and Crespin have identified the following:

- (a) Near Windalia Outcamp, six chains downstream from A.28, Lyndon River: *Fenestella propinqua*, de Kon; Crinoid ossicles, cf. *Platycrinus*; *Conularia warthi*, Waagen.
- (b) East end of Gnarrea Pool, Kialawibri Creek: *Plerophyllum australe*, Hinde; *Chonetes pratti*, Jno. Dav. *Orthis* (*Rhipidomella*) cf. *australis* McCoy also occurs here (identified by H. O. Fletcher); Spirifers are present, and a *Productus* is very abundant.

These fossils are from beds 1,500 to 1,600 feet below the top of the Lyons and from 500 to 700 feet above the lowest Permo-Carboniferous beds exposed on the Lyndon.

## (ii) Gascoyne Series.

The name Gascoyne Series as here proposed includes all the Permo-Carboniferous strata above the Lyons glacials. It consists of sandstone (55%), shale (30%) and limestone (15%); these percentages are based on outcrop measurements. The series becomes increasingly shaly to the north and west. The known thickness is between 4,250 and 5,000 feet. In ascending order the Gascoyne Series is divided into the Callytharra, Wooramel, Byro, Kennedy, and Wandagee Stages, each of which is described separately.

### *Callytharra Stage.*

#### (a) *Definition and General Relationships.*

In the type locality, Callytharra Spring on the Wooramel River, the beds (described by Rudd,<sup>(10)</sup> but also examined by the writer) consist of rather argillaceous limestone or highly calcareous mudstone, including foraminiferal, crinoidal, and shelly types. The thickness is 85 feet. In general appearance these beds strongly resemble the

Fossil Cliff beds of the Irwin River (shown on inset map, Plate III).

The Callytharra-Lyons contact has already been described.

The Callytharra-Wooramel contact is a particularly sharp one, well exposed over wide areas. There are many places where dip surfaces and sections of the contact can be examined. All of these show conformity. In the Wyndham and Arthur Valleys the top of the Callytharra is marked by a layer of limonite not more than half an inch thick or a bed of highly ferruginous sandstone a few inches thick.

(b) *Distribution and Type of Outcrop.*

From the Wyndham River in the south where these investigations commenced, to the Lyndon River in the north, where the Permo-Carboniferous sediments pass under a cover of Cretaceous, the Callytharra beds form an almost continuous outcrop, either as a defined range or series of ranges where faulting and folding have caused duplication. This is a distance of 130 miles. One continuous line of outcrop from the Wyndham to the Lyndon River is defined by the following points:

Fossil Hill, N.56 (Wyndham River); K.35 (Arthur River); Lyons River Homestead; one-quarter mile east of Mt. Sandiman shearing shed; about one mile west of K.49; Tambrong Pool (Minilya River). Commencing five miles south of Barragooda Pool on the Arthur River, this line of outcrop is paralleled by another at a distance of five to fifteen miles from it which passes through or near: K.34, five miles west of Mt. Sandiman Homestead; the Mt. Sandiman-Moogoorie motor road; K.51 on the Lyndon River.

There are at least four parallel outcrops of Callytharra crossing the Lyndon River:

- (1) K.51, three miles upstream from Williambury Pool.
- (2) Tambrong Pool, five miles below the junction of the north and south branches.
- (3) Kurrakootarrow (not on map), fourteen miles downstream from Tambrong Pool.
- (4) Rabbit-proof fence forming the boundary between Williambury and Middalya Stations. (Between Chubby Hills and Tambrong Pool, on map.)

The second and third of these extend to the motor road between Williambury and Middalya. From this point northwards to the Lyndon the Callytharra-Wooramel forms the dominant features in the landscape. One line of outcrop from K.55 to the junction of Kialawibri Creek and the Lyndon forms the Moogooloo Range. Another extends from K.52 to the south boundary of Mia Mia Station, where it merges into the Moogooloo Range, forming thence northwards an outcrop five miles in width. There is also an outcrop on a short range (not shown on existing published maps) between K.55 and K.52.

Throughout the area examined the Callytharra forms easily recognisable outcrops. As the common dip is westerly, the outcrop of the Callytharra beds (particularly that of the upper members) takes the form of ranges rising as much as 250 feet above the general level, with a scarp on the eastern side and a long dip surface on the western side. Erosion of the eastern scarp produces a typical topographic form; short spurs curved in plan and with a slope of thirty-five to forty degrees. These ranges of Callytharra beds have a characteristic greyish or yellowish-green colour, and as the ranges are commonly partly capped by sandstone of the Wooramel Stage, the colour contrast is quite a help in reconnaissance.

Erosion of the lower beds produces a grey-green surface strewn with marine fossils, some well preserved, and some fragmentary.

### (c) *Lithology and Thickness.*

In the southern part of the North-west Division the Callytharra Stage generally consists of an upper or flaggy type and a lower or shaly type. The upper consists of alternations of hard yellowish-green limestone and shaly beds from two to twelve inches thick. The lower section consists of soft calcareous shaly mudstone (with abundant *Fenestellidæ*) with few hard bands. Weathering of the upper section produces slabs suitable for flagging and building, for which purpose they have been used on some stations.

North of the Minilya River this twofold division is departed from in places. Thirteen miles south-east of Moogooloo a shaly zone about ninety feet thick separates two nearly equal flaggy portions, whilst at Moogooloo itself the upper flaggy beds are overlain by shaly limestone with hard lenticular calcareous bands at the top.

Except between Moogooree and K.51 on the Lyndon River the Callytharra yields marine fossils very abundantly. In this section the limestone, which dips steeply, is much harder and closer textured than usual.

Sections were measured at the following localities: N.56, Wyndham River; near K.35, Arthur River; near K.34, eleven miles north-north-east of K.35; Tambrong Pool, Lyndon River; Lamont's lease, thirteen miles south-east of Moogooloo; Moogooloo. (See Fig. 4.)

The sections give the thickness of the stage at the various localities and the approximate relative proportion of shaly and flaggy types. Owing to the bold nature of the outcrops it is possible to say from a general visual examination that the sections are representative of considerable lengths of outcrop on each side of the point of actual measurement. Definite thickening of the stage from the south-east to the north-west is indicated, and this is further emphasised by the fact that at Callytharra Spring, about sixty miles south of the Wyndham, its thickness is only eighty-five feet. The maximum thickness shown is 460 feet, but it is possible that at Moogooloo it is somewhat greater than this, as the Lyons-Callytharra Junction is obscured by sandhills. The Mia Mia Five Mile or Jam Thicket bore (No. 15) is known to have passed through the Callytharra. The log of this bore is not a good one, but the details available suggest a possible thickness of 690 feet for the Callytharra.

#### (d) *Palæontological Notes.*

F. Chapman's determinations of E. A. Rudd's collection from the type locality (Callytharra Spring), not previously published, are given below.

##### *Foraminifera.*

*Dentalina labiata*, *Dentalina* sp., *Spandelinoides striatoclavata*, *Trepeilopsis grandis*, *Calcitornella stephensi*, *Stacheia marginulinoides*, *Stacheia pupoides*, *Stacheia* sp., *Ammodiscus incertus*, *Ammodiscus* sp., *Palæobigenerina* sp., *Frondicularia woodwardi*, *Frondicularia* sp., *Ruditaxis rudis*, *Globivalvulina plicata*, *Tetrataxis conica*.

##### *Cœlenterata.*

*Dibunophyllum* (*Verbeekiella*) *talboti*, *Plerophyllum australe*, *Plerophyllum sulcatum*, *Plerophyllum gregoriana*, *Plerophyllum* sp., cf. *Zaphrentis* sp.

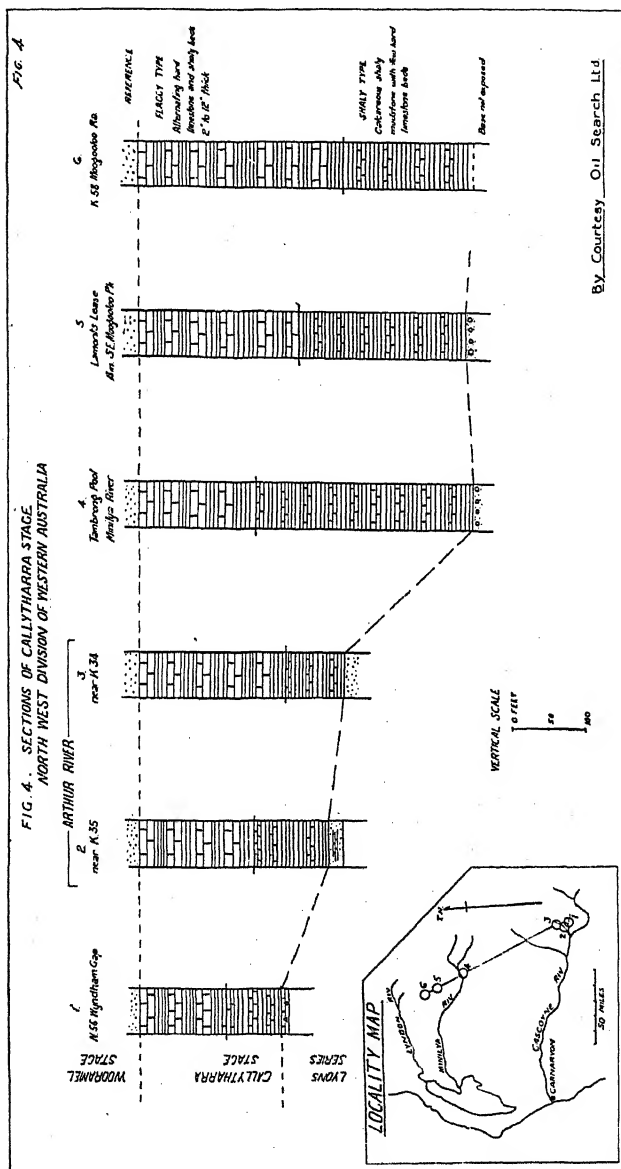


Fig. 4.—Comparative sections of *Callytharra* Stage.



*Polyzoa.*

*Evactinopora dendroidea*, *Evactinopora crucialis*, *Dybowskiella* sp., *Glyptopora* sp., *Coscinium australe*, *Trachypora* sp., cf. *Pachypora*, *Monilopora nicholsoni*, *Fenestella spinulifera*, *Fenestella pectinis*, *Rhombopora tenuis*, *Rhombopora multi-granulata*, *Acanthocladia* sp., *Ætomacladia ambrosioides*, *Streblotrypa etheridgei*, *Pinnatopora trilineata* var. *texana*, *Streblotrypa marmionensis*, *Polypora ampla*.

*Crinoidea.*

*Phialocrinus* sp., *Rhipidocrinus* sp., cf. *Cyathocrinus* sp., cf. *Hexacrinus* sp., *Platycrinus* sp.,

*Brachiopoda.*

*Spiriferella australasica*, *Cleiothyridina macleayana*, *Cleiothyridina* sp., *Chonetes pratti*, *Strophalosia* sp. nov., *Seminula* sp., *Seminula randsii*, *Derbya* cf. *bennetti*, *Reticularia lineata*, *Schwellwienella* sp., *Productus semireticulatus*, *Productus punctatus*, *Productus tenuistriatus* var. *foordi*, *Spiriferina* sp. nov., *Syringothyris exsuperans*, *Martiniopsis* sp., *Aulosteges baracoodensis*, *Spirifer hardmani*, *Spirifer* cf. *convolutus*, *Spirifer* cf. *duodecim-costatus*, *Spirifer* cf. *spiralis*, *Spirifer dubia*, *Spirifer musakheylensis* var. *australis*, *Dielasma hastata*, *Leptaena analoga*.

*Pelecypoda.*

*Nuculana* sp.

*Gasteropoda.*

*Warthia* sp., *Ptychomphalina maitlandi*.

*Cephalapoda.*

*Orthoceras* cf. *martinianum*.

*Ostracoda.*

*Healdia formosa*, *Healdia cuneola*, ? *Healdia* sp., cf. *Kelletella* sp., *Bairdia* sp., *Bairdia menardensis*, *Bairdia seminalis*, *Amphissites centronotus*, *Glyptopleura* aff. *costata*, ? *Cytherella* sp.

From his examination of fossils from the Wooramel district, Chapman concluded that the genera, more or less restricted to the Callytharra, are: *Plerophyllum*, *Monilopora*, *Dibunophyllum*, *Phialocrinus*, *Evactinopora*, *Syringothyris*, *Seminula*, *Cleiothyridina*, *Modiolus* and *Warthia*.

Recent work permits modification of this statement. *Plerophyllum* is now known to occur in both higher and lower beds, and *Cleiothyridina* and *Warthia* in higher beds.

The assemblage of Foraminifera is stated by Chapman to be similar to that of the Pokolbin beds of the Lower Marine Series of New South Wales, and to indicate a close relationship to the Pennsylvanian of Texas and Oklahoma, U.S.A.

The only fossil in the list of determinations of the author's specimens which is not represented in the above statement is *Spirifer rostralinus* var. *crassus*, which was collected at Tambrong Pool, Minilya River.

Additional forms identified by H. O. Fletcher in a collection by K. Washington Gray and the author are: *Linoproductus tenuistriatus* var. *foordi* (Eth.), *Productus* cf. *spiralis* Waagen, *Productus* cf. *indicus* Waagen.

### Wooramel Stage.

#### (a) Definition and General Relationships.

In the area examined in the North-west Division the Callytharra beds were found to be overlain conformably by about 150 feet of sandstone, certainly of Wooramel type. The sandstone in turn was overlain by sandy carbonaceous shale, giving a well defined upper limit. In this way the Wooramel Stage is delimited for the North-west Division. However, the carbonaceous shaly beds are themselves overlain by sandstone in places (not very different lithologically from those below), and it is not suggested that an exact correlation can be made on this basis with the Wooramel area.

To anticipate somewhat, the Wooramel sandstone is found to be much thinner than in the type area on the Wooramel River, and the overlying Byro beds to be much thicker. Field work between the Wooramel and Gascoyne is necessary to determine whether this is due to actual differences in thickness or differences in grouping.

On the Arthur and Wyndham Rivers the carbonaceous sandy shales appear to rest conformably upon the sandstone, but from the Minilya River northwards there is possibly slight difference in dip between the two. Places of special interest where this slight discordance appears to be present are K.55 and a cairn four miles south-easterly therefrom on Middalya Station, and Moogooloo Range (near the trig. station K.58 and also about twelve miles southerly from it).

(b) *Distribution and Type of Outcrop.*

The Wooramel sandstone forms a capping in many places to ranges of Callytharra limestone, and the areas of outcrop are thus generally so closely similar that it is unnecessary to describe those of the Wooramel in much detail.

The Wooramel sandstone forms bold outcrops between the Wyndham and Arthur Rivers. These extend south of the former river towards the Gascoyne, forming rather rough country in the locality known as "Boonawarra" on Bidgemia Station. North of the Arthur, the outcrops recognisable as Wooramel consist merely of small remnants, but it is possible that other of the sandstones in the faulted area between Moogooree and Williambury also belong to this stage. There are many small areas of outcrop associated with the faulted and folded Callytharra on the Minilya River. Quite extensive outcrops occur north of the river near K.52, and as previously stated the Wooramel sandstone caps the Callytharra on the Moogooloo Range from K.55 to the Lyndon River.

The colour contrast between the Wooramel sandstone and Callytharra limestone has already been mentioned. The ferruginous zones characteristic of the stage on the Wooramel are not much in evidence in the North-west Division.

(c) *Lithology and Thickness.*

In the North-west Division the Wooramel Stage consists wholly of sandstone, the principal type being medium to coarse grained, white to grey in colour when freshly broken, and usually micaceous. On the Gascoyne and its tributaries, the Wyndham, Arthur and Lyons, the Wooramel Stage characteristically consists of this type of sandstone 130 to 180 feet in thickness. In some good exposures on the Wyndham River the upper twenty feet were found to consist of thin bedded pitted sandstone with a few poorly preserved marine fossils. Two layers of white quartz pebbles, the largest three inches in diameter, were noted here also, within the upper fifty feet.

Sections were measured further north also at K.55 on Middalya Station, on Lamont's lease thirteen miles south-east of Moogooloo, and at Moogooloo itself (K.58). At K.55 the thickness is 250 feet, of which the upper 120 feet consists of the sandstone typical of the Gascoyne exposures,

cross-bedded at the top, underlain by 130 feet of argillaceous sandstone, with the bottom 100 feet very shaly.

On Lamont's lease the stage consists of 285 feet of medium to coarse grained sandstone, cross-bedded at the top, whilst at Moogooloo it is more like that at K.55.

In the type locality E. A. Rudd estimated the thickness of the Wooramel Stage to be 800 feet plus, made up of three types: a very fine grained micaceous sandstone laminated and resembling shale, rather massive with a subconchoidal fracture, and a coarse quartz grit. Ferruginous marine fossiliferous zones occur in the higher levels. The Wyndham section furnishes a parallel with this.

So far as the region described in this report is concerned, the Wooramel Stage, like the Callytharra, shows definite thickening from the south-east to the north-west from a minimum of 130 feet to a maximum of 285 feet.

The diagram, Fig. 5 summarises the foregoing observations

#### (d) *Palæontological Notes.*

Only a few poorly preserved marine forms were observed. F. Chapman's determinations of E. A. Rudd's specimens from the Wooramel area are:

*Polypora ampla*, *Fenestella* sp., *Strophalosia clarkei*, *Productus* cf. *undatus*, *Productus brachythærus*, *Tæniothærus subquadratus*, *Spirifer hardmani*, *Spirifer convolutus*, *Spirifer marcoui*, *Spirifer musakheylensis* var. *australis*, *Aviculopecten sprengi*, *Palæarca* cf. *costellata*, *Cardiomorpha blatchfordi*.

#### *Byro Stage.*

##### (a) *Definition and General Relationships.*

On Byro Station, Wooramel River, thin bedded sandstones and sandy shales overlie the Wooramel sandstone, and these E. A. Rudd named the Byro Formation.

On the Gascoyne and further north there is a considerable thickness of strata above the equivalents of the Byro beds, so that the upper limit requires definition. It is clear that the Byro beds are overlain by the sandstones which form the Kennedy Range. The Kennedy Range sandstones are a well defined lithological group, form one of the principal water-bearing beds of the North-west artesian basin, and stand out topographically from the underlying



Byro beds, so that the upper limit of the Byro Stage may be placed at their base.

On the Gascoyne River the contact is faulted, and along the western face of the Kennedy Range the contact relationships are not clear, due also to probable faulting. Along the east face of the Kennedy Range, however, the contact as examined on Middalya and Merlinleigh Stations appears to be a normal depositional one. A similar contact occurs on the south side of the Minilya River near K.54; on the Lyndon it is not exposed, being overlapped by Cretaceous.

The lower contact is well defined by the carbonaceous beds which rest upon the Wooramel sandstone. In places this contact is possibly disconformable (see also page 129).

(b) *Distribution and Type of Outcrop.*

The Byro beds occupy the valley of the Gascoyne from L.9 on Jimba Jimba Station upstream to a point above the Arthur and Wyndham Junctions. They also occur along the lower courses of these rivers. North of the Gascoyne the known outcrops of Byro beds form a wedge-shaped area pointing northwards, constituting the valley of the Lyons River for a distance of about twenty miles above its junction with the Gascoyne. There is also a narrow area of Byro beds which extends along the west side of the Kennedy Range to the north of K.39.

In the structurally disturbed area, between Merlinleigh Station and the Minilya River, Byro beds were not recognised. It is probable, however, that they occur in small patches here and there in this region.

Byro beds occupy the valley of the Minilya from the Williambury-Middalya boundary (rabbit-proof fence) to Coolkilya Pool on Wandagee Station, that is, for a distance of about forty miles. Over most of this length the outcrops are poor, but on Wandagee Station there are very good exposures of dark to carbonaceous sandy shales, sandy mudstones with calcareous lenses, and very thin-bedded sandstones. South of the river also, from Middalya towards Hill Springs, the upper beds are intermittently exposed, showing fossiliferous calcareous sandstones interbedded with dark shales. Dark to sandy shales may be seen resting on the Wooramel sandstone at K.55, K.52 and on the short range between these.

Between the Minilya and Lyndon Rivers there are few exposures. At the Burna Burna Hills (K.57) a small synclinal area of the upper sandy beds is preserved. On the Lyndon River the outcrop is largely obscured by overlapping Cretaceous and deposits of sand, but the lower carbonaceous sandy shales with calcareous concretions occur on Mia Mia Station in the neighbourhood of A.26, and a number of bores and wells which have penetrated these beds give good sections.

The Byro Stage consists largely of soft beds, and consequently occupies low lying country; the Byro plains of the type locality on the Wooramel River illustrate this. Similar plains occur on each of the three rivers, referred to above, namely Jimba Jimba Station on the Gascoyne, Wandagee and Middalya Stations on the Minilya, and Mia Mia Station on the Lyndon.

Exceptions to these soft beds in the Gascoyne sections are the sandy mudstones towards the top of the stage, the thin bedded sandstones about the middle, and the calcareous sandstones near the base. The sandy mudstones form good outcrops on the river banks, but not elsewhere; the thin bedded sandstones also are well exposed in the river, and form low ridges in the surrounding country. The lower calcareous sandstones form low but distinct strike ridges in the vicinity of N.56 on the Wyndham and south-west of K.35 on the Arthur River.

On the Minilya the most prominent outcrops away from the river sections are the sandy mudstones with calcareous lenses at the top of the stage. On Wandagee Station, between Cundlego Rocks and the Barrabiddy Hills, these form low wall-like outcrops ten to fifteen feet above otherwise featureless plains.

### (c) *Lithology and Thickness.*

The following is a section compiled from measurements on the Gascoyne and the lower Wyndham Rivers:

#### *Section of Byro Stage, Gascoyne and Wyndham Rivers.*

##### *Descending Order.*

Feet.

— Kennedy stage.

- (a) 400 Mainly clay shale with sandy mottled shale and some shaly sandstone. *Chonetes prattii* abundant.

- (b) 560 Sandy mudstone with richly fossiliferous calcareous zones, argillaceous sandstone and dark sandy shales. *Spirifer byroensis* common.
- (c) 560 Thin bedded (and current bedded) micaceous sandstone, reddish-brown to green in colour; alternating with sandy micaceous to carbonaceous shale. Sandy concretions one to two inches in diameter and *Deltopecten* aff. *subquinguelineatus* common. *Tribrachio-crinus* sp. abundant at Gascoyne Junction.
- (d) 250 Shaly mudstone and dark shale with few fossils. Possibly partly freshwater.
- (e) 125 Fine to medium grained soft white sandstone; thin bedded. No fossils observed.
- (f) 125 Thin bedded shaly and platy sandstone with dark to sandy shale. Poor outcrop.
- (g) 265 Flaggy, pitted limestone and calcareous sandstone in alternating beds five to ten feet thick. Small glacial erratics at top.
- (h) 15 Highly carbonaceous sandy shale.  
— Wooramel Stage.

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2,300

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On the Arthur River the lowest beds were independently measured:

Feet.

200 Calcareous sandstone and sandy limestone; thin bedded sandstone and sandy shale. Thin bed of *Callytharra* type limestone at top. Ripple marks common;

15 Highly carbonaceous shale.

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215

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The beds of group (b) in the Gascoyne River section appear to be very similar to those at Middle Camp on the Wooramel. They contain *Spirifer byroensis* very abundantly. Group (a) also contains beds examined in thin section by F. Chapman and described by him as "carbonaceous shales with probable plant remains". The Jimba Jimba sandstones (c) are distinguished from any other considerable group in the Permo-Carboniferous



sequence by their paper-thin bedding, spherical sandy concretions, and the abundance of the fossil *Deltopecten subquiquelineatus*. They are highly micaceous and brown to green in colour. Crinoid calyxes (*Tribrachiocrinus* sp.) were found well preserved in large numbers in outcrops of these beds in the river in front of the hotel at Gascoyne Junction.

The soft white sandstone (e) has been observed only at the one locality, namely the V-shaped area between the Wyndham and Arthur Rivers. These sandstones contain numerous small calcareous concretionary bodies one-quarter inch in diameter (determined by T. Hodge Smith).

The alternations of beds five to ten feet thick (g) make fair outcrops parallel to the Wooramel sandstone, and some of the beds are sufficiently persistent to be traceable for considerable distances.

The carbonaceous shale (h) is chiefly of value in defining the base of the stage and the top of the Wooramel sandstone. In the Wyndham River this bed is highly carbonaceous, and resembles a coal seam in outcrop.

About 120 feet of the upper portion of the Byro beds are exposed beneath the upturned edges of the sandstones on the west face of the Kennedy Range, about seven miles northerly from K.39. The details are much obscured by talus, cemented in places, and remnants of Cretaceous, but it can be seen that the strata are mainly clay shales with abundant spirifers.

The Byro Stage as exposed on the Minilya River is divisible into an upper portion consisting of mudstone, sandstone, and shale, and a lower consisting largely of dark to carbonaceous shale and shaly sandstone, in which *Chonetes* spp. occur in large numbers. The lower beds, which were first noted by Gibb Maitland,<sup>(5)</sup> were traversed between Wandagee homestead and Coolkilya Pool. They are gently folded and disturbed by small faults.

The following is a section of the upper portion of the Byro Stage, measured in the Minilya River, Wandagee Station.

*Section, upper part of Byro Stage, Wandagee.*

*Descending Order.*

Feet.

50 + Sandy shale.

40 Highly argillaceous sandstone to sandy shale with thin-bedded sandstone.

- 25 Gypseous shale.
- 15 Highly argillaceous sandstone to sandy shale with thin-bedded sandstone.
- 110 Thin-bedded sandstone, current bedded and with sandy shale.
- 110 Thin-bedded sandstone.
- 60 Sandy shale with ferruginous concretions and lenses of very thin-bedded sandstone.
- 150 Thin-bedded sandstone and very argillaceous sandstone.
- 70 Shale, sandy towards the top.
- 130 Thin-bedded sandstone and sandy mudstone with calcareous lenses.
- 40 Thin-bedded sandstone and argillaceous sandstone.
- 50 Carbonaceous sandy shale.
- 130 Massive sandy mudstone with large lenses of hard calcareous sandstone (Cundlego Rocks).
- 65 Thin-bedded sandstone and carbonaceous shale.
- 110 Sandy mudstone with large lenses of calcareous sandstone.

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1,155

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The Wandagee No. 1 bore commenced approximately at the base of the foregoing section, and passed through 1,315 feet of strata as follows :

*Wandagee No. 1 Bore.* Driller's log. Comments in parentheses.

Feet.

- 728 Dark blue shale with bands of sandstone.
- 3 Hard sandstone.
- 86 Dark blue shale with hard bands.
- 69 Hard sandstone with thin bands of shale.
- 164 "Slate" (probably well bedded hard shale).
- 65 Black shale with hard sandstone bands.
- 20 Grey sandstone with small bands of shale.
- 25 Hard grey sandstone.
- 9 Black shale with hard bands.
- 7 Hard grey sandstone.
- 6 Sandstone and white quartz.

- 9 Black shale with hard bands.  
 24 Sandstone with white quartz (probably  
 Wooramel sandstone).

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1,215

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The thickness of Byro beds given by the Wandagee sections is 2,330 feet.

The lower Byro beds, consisting of carbonaceous sandy shales with thin beds of sandstone, are exposed on the Lyndon River. Near the base the section is somewhat like that at K.55. At Moogooloo and southwards therefrom 100 feet of sandy beds were noted above the basal carbonaceous shales, but the details were obscured by talus. Charley's Well on Mia Mia Station passed through 105 feet of dark shales near the base of the Stage. A *Sanguinolites* was found on the dump at this well.

On the north side of the Lyndon the following bores on Mia Mia Station give partial sections of the Byro Stage :

Jam Thicket or Five Mile (No. 15), Four Corners or No. 1 Artesian (No. 12), No. 5 Artesian (No. 14), No. 6 Artesian (No. 8), and No. 2 Artesian (No. 10).

Still further north are the Winning No. 2 Bore (No. 7) and the Cardabia No. 1 (No. 5) and No. 2 (No. 4) Bores, which give some information concerning the Byro Stage in an area occupied at the surface by Cretaceous rocks.

Where the bores have passed through Cretaceous shales (the basal sands being missing or not logged) into shales of the Byro Stage, it is difficult to draw a line of distinction. The Mia Mia No. 5 (No. 14) and No. 6 (No. 8) Bores proved from 500 to 630 feet of the upper part of the Byro beds, the relevant section of the driller's log of No. 5 Bore between the depths of 655 and 1,281 feet being as follows :

Feet.

- 49 Firm slaty shale with bands of firm sandstone.  
 125 Hard grey sandy shale.  
 228 Grey shale with bands of grey rock. (Calcareous sandstone ?)  
 19 Hard fine sandstone.  
 19 Hard sandstone with bands of grey rock.  
 69 Grey shale with bands of sandstone.  
 23 Grey shale and rock.  
 19 Grey shale with bands of sandstone.  
 40 Grey shale with bands of sandstone.

24 Sandstone.

11 Grey rock.

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626

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The Jam Thicket or Five Mile Bore (No. 15) commenced in dark shales and continued in strata of much the same type for 930 feet.

Fig. 6 gives comparative sections of the Byro Stage in the Gascoyne, Minilya and Lyndon Valleys.

Even allowing for the fact that some of the lower beds may prove to belong to the Wooramel Stage, the Byro Beds show an increased thickness as compared with the type area, but from the Gascoyne northwards the thickness may be fairly constant.

The proportion of shaly beds in the Gascoyne Section is greater than in the Wooramel, and this increase becomes more marked the farther north one goes.

#### (d) *Palæontological Notes.*

The Byro Beds, generally speaking, are characterised by a number of restricted zones in which fossils are very abundant, separated by zones in which fossils are found rarely, if at all. Such fossiliferous zones are the Jimba Jimba sandstones with abundant *Deltopecten subquiquelineatus* McCoy, and *Tribrachiocrinus* sp., the sandy limestones towards the top with *Linoproductus tenuistriatus* found on Middalya Station, the *Spirifer byroensis* calcareous sandstones on the Gascoyne and the recurring thin beds crowded with *Chonetes pratti* and *Chonetes hardrensis* on the Minilya and Gascoyne.

The following localities on the Gascoyne River are arranged in ascending stratigraphical order, and comprise units (a), (b) and (c) of the Gascoyne sequence described on pages 134 and 135 and illustrated in Fig. 6.

- (1) In front of Gascoyne Junction Hotel: *Tribrachiocrinus* sp., *Chonetes hardrensis* Phil., var. *cracowensis* Eth., cf. *Warthia* sp.
- (2) Jimba Jimba Homestead: *Deltopecten subquiquelineatus* McCoy.
- (3) 2.9 miles west of Jimba Jimba Homestead: *Chonetes hardrensis* Phil. and crustacean tracks (?).
- (4) 3.0 miles west of Jimba Jimba Homestead: Probable seed-like bodies.

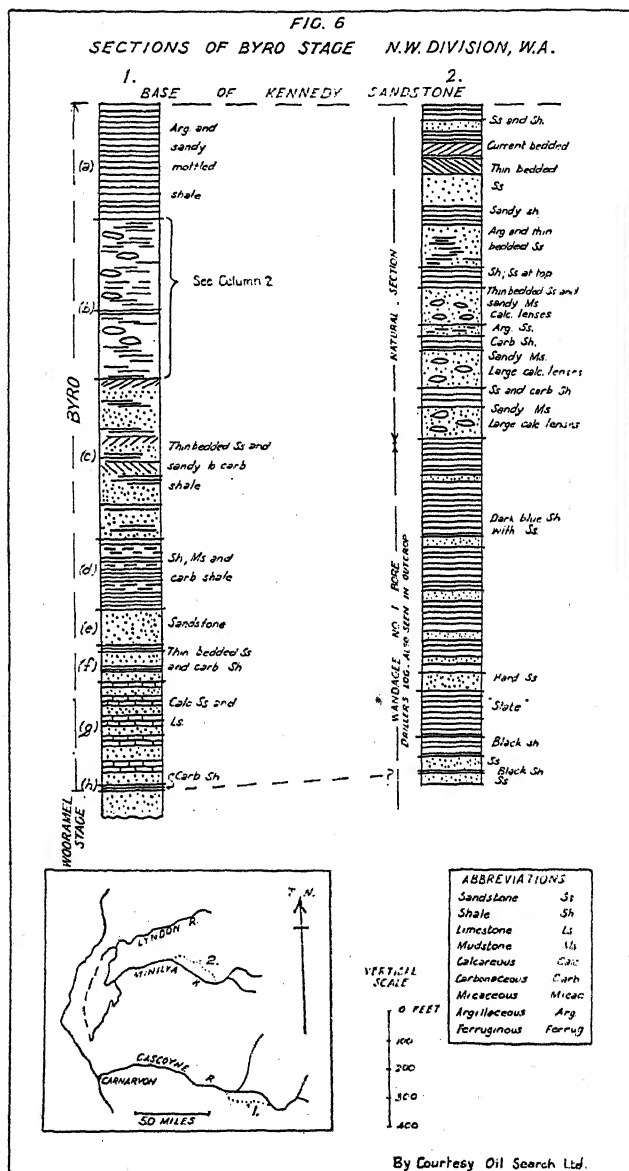


Fig. 6.—Comparative sections of Byro Stage.

- (5) 3.4 miles west of Jimba Jimba Homestead: *Chonetes pratti*.
- (6) 4.5 miles west of Jimba Jimba Homestead: *Aviculopecten* sp.
- (7) 1.0 mile east of mouth of Salt Gully: *Spirifer convolutus* Phil., attenuate variety.
- (8) 0.75 mile east of mouth of Salt Gully: *Spirifer byroensis* McCoy, *Spirifer rosalinus* var. *aurita* Hosking.

From shale beds immediately below the base of the Kennedy sandstone, seven miles northerly from K.39, the following were collected: *Spirifer* sp., *Strophalosia clarkei* Eth.; from Bulgadoo Pool, Minilya River: *Chonetes* cf. *hardrensis* Phil., *Chonetes pratti* Dav.; and from Charley's Well, Mia Mia., *Sanguinolites* sp. The above determinations are by F. Chapman and Irene Crespin.

Maitland (<sup>(6)</sup>, p. 36) records *Chonetes pratti* Dav., *Aviculopecten tenuicollis* Dana, and *Ptychomphalina maitlandi* Eth. fil. from micaceous sandstones which occur in the upper part of the Byro on the Minilya River at Wandagee Station.

F. G. Clapp (<sup>(7)</sup>, p. 55) collected fossils from a locality five miles west of Gascoyne Junction (i.e. approximately from the same beds as at No. 6 in the above list), which were identified by the late W. S. Dun as "*Productus bellus*" (*Linoproductus cancriniformis*), *Spirifer* cf. *lata* (Eth. and Foord—not McCoy; will be renamed *maitlandi*), *Plerophyllum australe* Hinde, *Chonetes* sp. (*pratti*?).

*Spirifer* cf. *musakheylensis* and *Spirifer marcoui* were also collected by Clapp from beds fairly high in the Byro on the east side of the Kennedy Range near Merlinleigh.

Lucy Hosking (<sup>(16)</sup>, p. 9) recognised *Deltopecten subquinelineatus*, apparently rather restricted in vertical range, in collections made by Talbot, Feldtmann and Hobson on the Wooramel from beds above the Callytharra (now known to be the Byro). In F. Chapman's list of determinations in the Rudd and Dee collection this fossil is also restricted to the Byro.

### Kennedy Stage.

#### (a) Definition and General Relationships.

Every observer in the region has commented on that distinct topographic feature, the Kennedy Range. It is a deeply dissected, approximately flat-topped block,

extending from the Gascoyne to the Minilya River, and rising to a height of 300 to 400 feet above the surrounding country (1,200 feet above sea-level). It is composed almost entirely of sandstone. This block was examined at intervals around its margin and the fact established that the sandstones which compose the range overlie the more shaly strata of the Byro Stage, the contact being conformable. These sandstones are named the Kennedy Stage.

It may be mentioned here that the alignment of the Moogooloo, Kennedy and Carrandibby Ranges has suggested to some observers<sup>(5) (7)</sup> a more or less continuous line of outcrop of the same lithological unit, but Rudd and Dee found the Carrandibby Range to be composed of Pre-Cambrian rocks, and the Moogooloo Range, as already stated, consists of Callytharra limestone and Wooramel sandstone, which have been brought more or less into linear arrangement with the Kennedy Range by faulting.

The flat top of the Kennedy Range is an erosion surface, and nowhere upon it do there appear to be any higher Permo-Carboniferous rocks preserved. Sandhills are found on the top of the range on Merlinleigh Station (first recorded by F. G. Clapp<sup>(7)</sup>), and Mr. J. Thompson, of this Station, has picked up several internal casts of a shell identified by F. Chapman as *Aturia* sp. (Eocene to Miocene) from a locality two miles north-east of Merlinleigh shearing shed.

Gibb Maitland<sup>(5)</sup> commented on the lithological resemblance of the rocks of Wandagee Hill to the Kennedy Range sandstones, and there is little doubt that they belong to the same Stage. At Wandagee Hill the conformable lower contact with the Byro beds is well shown, a fossiliferous horizon marking the top of the lower stage. Here again, however, there is no evidence of the existence of higher Permo-Carboniferous beds, since Cretaceous green shales are faulted against the Kennedy beds at this point. The spoil from Cundy Dam, nearby, yielded the beautifully preserved belemnites described by Glaupert.<sup>(17)</sup>

At Coolkilya Pool, on the Minilya River, seven miles north of Wandagee Hill, is a section showing Byro beds passing upwards into sandstones, which in turn are overlain conformably by a considerable thickness of shale with rather distinctive Permo-Carboniferous fossils. These sandstones cannot be followed directly to Wandagee Hill,

but some of the underlying Byro beds can be traced in such a way as to suggest the identity of the sandstone at Coolkilya with that at Wandagee Hill, and a valuable check is afforded by the Wandagee No. 1 (No. 34) Bore, one and a half miles north-west of the hill, which was put down almost wholly in Byro beds. (See Fig. 8.)

(b) *Distribution and Type of Outcrop.*

The principal area is the Kennedy Range, which extends for sixty-five miles from K.39 on the Gascoyne to K.54 on the Minilya, and is from five to fifteen miles wide. There are no tracks through this region, but its margins are readily accessible from a number of points. Other small outcrops occur at intervals from the bend at the 66 mile post in the rabbit-proof fence (three miles east of Paddy's Outcamp on map) to Wandagee Hill, and at Coolkilya Pool on the Minilya River.

North of the Minilya it is probable that the Kennedy beds are completely obscured by Mesozoic to recent deposits.

South of the Gascoyne, outcrops of these beds have not been recognised, but it is worth noting that E. A. Rudd provisionally assigned 800 feet of sandstone met with in the deep bore on Byro Station to a stratigraphical position above the Byro beds.

Since the Kennedy sandstone forms one of the most important aquifers in the North-west Basin, it can be readily identified in a large number of the deep bores put down in the coastal region, west and north-west of the principal lines of outcrop.

In outcrop there is little to distinguish the Kennedy from the Wooramel sandstone. The former is perhaps characterised by an abundance of ferruginous concretionary material in its lower portions. As mentioned by previous observers, fossil casts are commonly ferruginous also, but this type of preservation is by no means restricted to the Kennedy beds. Rudd<sup>(11)</sup> refers to such fossils in the Wooramel sandstone of the type locality, and on the recent expeditions ferruginous casts have been collected by the author from both this formation and the Callytharra.

(c) *Lithology and Thickness.*

Since the top of the Kennedy Range is an erosion surface, most of the sections measured there are incomplete, and the



logs of the bores on the lower Gascoyne furnish the best data.

A number of sections were measured around the margins of the Kennedy Range from which two are selected, as follows :

Jimba Jimba-Mooka boundary, west face of range, seven miles northerly from K.39.

Feet.

- 140 + Blocky dense highly ferruginous sandstone.
- 80 Well bedded white to grey sandstone, the white bands highly micaceous.
- 160 Fine grained sandstone, argillaceous in places.
- 20 + Fine yellowish-brown sandstone with *Strophalosia clarkei* and *Aviculopecten tenuicollis*.

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400 +

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At Wandagee Hill the thickness preserved is 350 feet. Near the top of the hill are numerous poorly preserved fossils, including *Aviculopecten tenuicollis* and *Spirifer* sp. The following section is exposed at Coolkilya Pool, on the Minilya River :

Feet.

- 146 Massive argillaceous sandstone to thin-bedded sandstone.
- 39 Shale.
- 90 Thin-bedded sandstone and sandy mudstone with thin shale beds.
- 230 Massive to shaly and micaceous sandstone with ferruginous concretions up to three feet in diameter.

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505

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The shaly nature of this section suggests that it may be difficult to identify the Kennedy beds in bores to the north.

A few bore sections may be briefly referred to.

The Boolathanna No. 6 (No. 47) and the Pelican Hill (Bibbawarra) (No. 52) bores proved 660 feet of Kennedy sandstones, and the Brickhouse No. 1 Bore (No. 54) 700 feet, of which a number of core samples have been preserved and are available for examination at the office of the Geological Survey of Western Australia. Following is a

section of these beds compiled from examination of the core samples of the Brickhouse No. 1 Bore (No. 54).

*Brickhouse Bore, 1,933 feet to bottom.*

Feet.

214 Coarse arkosic sandstone to grit; much subidiomorphic, glassy quartz. Small white quartz pebble.

378 Medium to coarse red and greenish grey micaceous sandstone.

66 Red micaceous shaly sandstone.

43 Fine grained sandstone.

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701

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The Minilya No. 3 (No. 24) (Chirrita) bore passed through 581 feet of strata described by the driller as "sandstone and hard rock" (the latter probably hard fine grained sandstone), from 1,674 feet to the bottom of the bore hole.

(d) *Palæontological Notes.*

Fossils are not very abundant in the Kennedy sandstone, but in places ferruginous bands are found which contain a large number of a few species such as those recorded by Maitland (<sup>(6)</sup>, p. 34) from the top of the south end of the Kennedy Range, *Spirifer* sp., *Productus* sp., and *Strophalosia*.

*Strophalosia clarkei* and *Aviculopecten tenuicollis* (identified by H. O. Fletcher) occur fairly abundantly in the basal yellowish-brown sandstone on the west side of the Kennedy Range, two and a half miles south-south-west of Mooka Spring, and from ferruginous beds near the base of the Stage (ten miles south-west of K.34) F. Chapman identifies *Spirifer byroensis* Glauert, *Spirifer musakheylensis* Dav., *Spirifer musakheylensis* var. *australis* Foord, *Cardiomorpha blatchfordi* Hosking.

H. O. Fletcher has also identified *Aviculopecten tenuicollis*, collected from beds near the top of Wandagee Hill.

*Wandagee Stage.*

Downstream from Cookkilya Pool on the Minilya River are excellent exposures of shales and shaly sandstones with *Chonetes*, *Aulosteges* and *Spirifers*. These rest directly

and conformably on the sandstones of the Kennedy Stage, and are overlain by fossiliferous marine Cretaceous.

The logs are available of a series of artesian and sub-artesian bores well spaced from Wandagee Station to Minilya Station, and thence north and south in the deeper part of the basin. It is thus possible to identify the Wandagee Stage in a number of bores and confirm its lithology.

Thus, although little is seen of the Wandagee beds in outcrop, there is good evidence that they formerly extended over a considerable area in the North-west Basin. -

#### (a) *Lithology and Thickness.*

The Minilya River downstream from Coolkilya Pool provides the type section:

##### Descending Order.

Feet.

- |       |   |
|-------|---|
| 385 + | Shale. Carbonaceous and sandy, with thin beds of very thin-bedded sandstone. Most sandy towards the top. Marine fossils.  |
| 385   | Argillaceous sandstone and soft sandy mudstone with calcareous and ferruginous concretionary zones. <i>Aulosteges ingens</i> and <i>Spirifer rostratus</i> var. <i>crassus</i> , common, <i>Chonetes pratti</i> , <i>Spirifer marcoui</i> . |
| 500   | Clayey shales with calcareous and ferruginous concretions, dark towards the base.   |

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1,270

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The Pelican Hill (Bibbawarra) Bore (No. 52) passed from glauconite sands at the base of the Cretaceous into the Wandagee beds at a depth of 1,406 feet. The following section is compiled from an examination of the cores and of notes from office files made available by F. Forman, Government Geologist. (Determinations of fossils are by R. Etheridge, Jnr.<sup>(25)</sup>)

Thickness

in

Feet.

- |    |  |
|----|--|
| 32 | Shaly limestone with <i>Aviculopecten</i> sp., <i>Spirifer</i> sp. |
| 8  | Grey to green hard shale.  |
| 50 | Mainly fossiliferous limestone with thin shale bands.              |

- 150 Dark grey shale and crystalline fossiliferous limestone.
- 50 Fossiliferous crystalline dark grey limestone.
- 315 Hard dark green clay shales.
- 50 Calcareous sandstone.
- 85 Green and grey shale with sandy bands.
- 30 Calcareous sandstone.
- 130 Green to grey compact clay shale with bivalves and small dendroid coral, probably *Monticulipora*.
- 43 Hard siliceous grey shale.

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943

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The bottom of this section is at depth 2,350. The remaining 660 feet is in the Kennedy sandstone.

The Boolathanna No. 6 Bore (No. 47) also proved a section of these beds between the depths of 1,472 and 2,920 (i.e. about 1,450 feet thickness), the upper portion including limestone. It is of interest to note that below depth 2,095 feet the bore passed through three feet of quartz. This may be an erratic.

#### (b) *Palæontological Notes.*

The forms listed below and identified by Chapman and Crespin are all very abundant at the type locality on the Minilya River, Wandagee Station, downstream from Coolkilya Pool :

*Chonetes pratti* Dav., *Stenopora* sp., *Spirifer convolutus* Phil., *Spirifer rosalinus* var. *crassus* Hosking. Beautifully preserved specimens of *Aulosteges ingens* and *Spirifer marcoui* (identified by H. O. Fletcher) are also quite common.

#### The Winnemia Section.

Along and adjacent to the Gascoyne River at the south end of the Kennedy Range, and four miles upstream from Winnemia are some very interesting exposures bounded by faults. The section exposed in the cliffs on the south bank of the Gascoyne River, in descending order, is as follows :

*Section left bank Gascoyne River, four miles upstream from Winnemia.*

Feet.

- 24 Earthy limestones with hard bands like Callytharra.

- 12 Shaly limestone with large fossil shells.
- 6 Earthy limestone with *Productus foordi*.
- 18 Grey to brown pitted sandstone.
- 120 Hard massive current-bedded sandstone.
- 10 Argillaceous sandstone.
- 20 Highly fossiliferous limestone and calcareous sandy shale (like *Callytharra* lithologically).
- 110 Grey to yellowish-brown thin-bedded sandstone with pittings and possible fossil imprints, ripple marked.
- 70 Sandy shale.
- Lenticular bed calcareous sandstone with a few marine fossils.
- 155 Highly argillaceous sandstone, sandy shale.
- 120 Thin-bedded sandstone, argillaceous in places.
- Shale.

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665

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Fossils collected from the upper limestones have been identified by F. Chapman as follows :

- (1) *Oleiothyridina macleayana* Eth. fl., *Polypora* sp., *Dybowskiella* sp., *Reticularia* sp., *Chonetes pratti* Dav., *Productus foordi* Eth. fl.

and from the lower :

- (2) *Dibunophyllum* (*Verbeekiella*) *talboti* Hosking, *Plerophyllum australe* Hinde, Crinoid stems and ossicles, *Fistulipora incrustans* Moore, *Aetomacladia ambronis* Bretnall, *Fenestella pectinus* Moore, *Fenestella modesta* Ulrich, *Rhombopora tenuis* Hinde (also var.), *Stenopora tasmaniensis* Lonsdale, *Polypora* sp.

On the north bank between K.39 and L.9 the section exposed is :

Feet.

- Shale.
- 5 Lenticular sandstone bed.
- 250 Mainly green gypseous shale with thin lenticular sandstone bands and erratics up to two feet.
- 75 Thin-bedded friable sandstone.
- 75+ Sandy gypseous shale with erratics.

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430+

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There seems little doubt that there is a fairly complete sequence from the base of this section to the top of that first given. The main question is, what is its relation to the Kennedy sandstone at K.39? In view of the general similarity between the sequence and the established Permo-Carboniferous succession in this region, and also the Callytharra aspect of the lower limestone fauna it is concluded that the Lyons-basal Byro beds are represented. This implies that the fault near K.39 is a steep overthrust with a considerable throw. No faults of this magnitude have been observed or suspected anywhere else in the region. If the fault is an overthrust of this magnitude it is certainly Pre-Cretaceous.

Adopting the explanation that the Lyons-Byro sequence is present, it implies that from east to west in a distance of thirty-five miles the Callytharra has thinned from 180 feet to 25 feet, and the unfossiliferous calcareous sandstones and sandy limestones at the base of the Byro, as exposed on the Arthur and Wyndham Rivers, have passed into limestone of Callytharra type.

On the other hand the fault may be a small normal one, and the whole sequence be referable to the Wandagee beds. The section has certain resemblances to the Wandagee sequence, as proved by bores. Such an explanation would, however, be at variance with the palæontological evidence.

#### Irwin River Section.

The Irwin River section was first described by Campbell<sup>(18)</sup> and later by Woolnough and Somerville.<sup>(19)</sup> The latter authors suggest the following subdivision of the Permo-Carboniferous in this locality:

- (1) Upper Marine, (2) Coal Measures, (3) Fossil Cliff Beds, (4) Olive Shales—Cephalopod Horizon (*Metalegoceras jacksoni*), (5) Buff Beds, (6) Bull Paddock Limestone, (7) Grey limestone, (8) Spheroidal marls, (9) Glacial beds, (10) Sub-glacials, (11) Basal grits and boulder clays.

Some sections were measured by the author, and general observations made which are summarised below. (The numbers at the side indicate the same units as those named by Woolnough and Somerville.) The thickness of the Olive Shale is from measurements kindly made available by E. de C. Clarke, which agrees well with that of

Woolnough and Somerville. The thickness of other units is not stated by these authors.

| Thick-<br>Unit. ness. | Lithological Character.  |
|-----------------------|--|
| 1 300                 | Shale varying from sandy and micaceous to brown and carbonaceous, and with sandstone bands up to 18 inches in thickness near base. Erratics of granite, gneiss and quartzite towards base.   |
| 2 250                 | <p>Coal Measures. The following section was measured in the north branch of the Irwin :</p> <p>8 ft. Thinly bedded sandy shale.</p> <p>10 ft. Argillaceous sandstone with erratics.</p> <p>2 ft. Sandy shale.</p> <p>9 in. Grit.</p> <p>3 ft. Dirty coal seam.</p> <p>4 ft. Argillaceous and carbonaceous sandstone.</p> <p>10 ft. Thinly bedded carbonaceous and sandy shale.</p> <p>10 ft. Thinly bedded argillaceous sandstone.</p> <p>5 ft. 6 in. Coal and carbonaceous shale.</p> <p>12 ft. + Clay shale.</p> <p>50 ft. Argillaceous sandstone.</p> <p>25 ft. Highly carbonaceous shale.</p> <p>28 ft. Coarse and carbonaceous sandstone.</p> <p>69 ft. Fine grained sandstone.</p> <p>1 ft. 6 in. Carbonaceous sandy shale.</p> <p>8 ft. Current-bedded sandstone.</p> |
| 3 75                  | <p>Fossil Cliff Beds. The section at the type locality is :</p> <p>1 ft. 6 in. Carbonaceous sandy shale.</p> <p>10 ft. Fine grained carbonaceous sandstone with pyritic concretions.</p> <p>1 19 ft. Sandy carbonaceous mudstone. Marine fossils abundant.</p> <p>0 to 4 ft. Highly ferruginous sandstone.</p> <p>40 ft. Carbonaceous sandy mudstone. Marine fossils.</p> <p>2 to 4 ft. Gypseous sandy mudstone.</p>   |
| 4 1,000               | Sandy clayey shales with occasional erratics and calcareous concretionary zones.   |
| — —                   | Cephalopod horizons (more than one suspected).   |

- 5      50 Structureless sandy mudstones and shales with calcareous zones.
- 6      20 Shales with numerous calcareous concretions.
- 7 & 8   450 Clayey shales with zones of concretions, some calcareous and with marked cone-in-cone structure. A few large boulders of granite and quartzose rocks which are probably erratics.
- 9      Not known Clays with numerous glacial erratics.
- 10     „      Soft greenish-grey shales.
- 11     „      Conglomerates and grits with erratics.

Summarising further it will be seen the section is made up as follows :

- 300 Shale, largely carbonaceous and with glacial erratics (marine).
- 250 Shale, sandstone and coal seams (freshwater).
- 75 Highly fossiliferous (marine) calcareous mudstone to shaly limestone.
- 15,20 Shale with some sandy mudstone ; calcareous concretions (contains cephalopod horizons).
- Glacial beds and shales.

#### Correlation of North-west Basin, Wooramel and Irwin River Sections.

Any field worker proceeding from the Irwin River to the Wooramel, thence to the Gascoyne and northwards must be impressed with the general similarities in the Permo-Carboniferous succession at these localities. The major units into which the sequence has been divided indicate something more than lithologic differences at least in so far as the lower part of the section is concerned.

In each instance there is evidence at the base of the section of glacial conditions extending over a long period of time. Passing upwards, glacial conditions are less in evidence, extensive shale beds with fossiliferous calcareous beds are found, and above these lie richly fossiliferous marine limestones and calcareous mudstones, which in the northernmost exposures attain a thickness of not less than 460 feet. Here is evidence of geological environments which cannot be regarded as local, but which must have prevailed over a large part of the earth's surface.

The case for correlation of the glacials has been well stated by Maitland,<sup>(4)</sup> and the discovery that these beds



have a thickness of not less than 2,000 feet in the North-west strengthens the argument, because it is a record of glacial conditions on a grand scale which must have been represented far and wide. Indeed the Lyons beds are continuous from the Wooramel to the Lyndon, a distance of 150 miles, and they have been found<sup>(4)</sup> on the Murchison intermediate between the Wooramel and the Irwin.

The correlation of the glacials carries with it the almost inevitable corollary that the Fossil Cliff beds of the Irwin River are the representatives of the Callytharra limestone of the Wooramel River and North-west sequences.

They are certainly strikingly similar, and have many fossil forms in common. Indeed, on the latter evidence alone Miss Lucy Hosking suggested a correlation between the beds at Callytharra Spring and Fossil Cliff.<sup>(16) (20)</sup>

This conclusion is apparently not supported by F. Chapman, who in a recent statement<sup>(21)</sup> refers to the Callytharra fauna as being Upper Carboniferous and the Fossil Cliff beds as Lower Permian. He also states, however, that the foraminiferal phase of the Fossil Cliff beds has "many species in common with both the Pennsylvanian and Permian of Texas (Upper Carboniferous to Middle Permian)". This statement does not preclude the possibility of correlating the Callytharra and Fossil Cliff beds. Sir Edgeworth David placed the Fossil Cliff beds in the Lower Permian,<sup>(14)</sup> but did not refer to any North-west horizons other than the Lyons glacials.

If the Callytharra-Fossil Cliff correlation is accepted, the 1,520 feet of shaly strata in the Irwin River section (Olive Shale, Buff Beds, Bull Paddock limestone and grey limestone and Spheroidal marls), with their Cephalopod (*Metalegoceras*) horizons, must be correlated with the shales (about 300 feet thick) constituting the upper part of the Lyons Series in the North-west Division.

The general nature of the sedimentation above the Fossil Cliff beds on the Irwin River and above the Callytharra stage in the North-west Division suggests that the Wooramel and Byro Stages are represented on the Irwin, and that the highest beds, of the North-west, those of the Kennedy and Wandagee Stages, either were not deposited in the south or else were removed by denudation prior to the deposition of the Jurassic.

The units above the Fossil Cliff beds on the Irwin River are the Coal Measures and the Upper Marine.

The lower portion (200 feet) of the Coal Measures consists almost entirely of sandstones; these are overlain by about fifty feet of shales with coal seams, above which are the dark shales of the Upper Marine with a few erratics.

Comparing this with the North-west section, there are 130 to 800 feet of sandstone of the Wooramel Stage, overlying the Callytharra. On the Wyndham and Arthur Rivers at least, this sandstone is overlain by the ten to fifteen feet of highly carbonaceous shale at the base of the Byro Stage. Higher still in the Byro Stage are marine strata, which on the Wyndham contain a few small erratics as do the Irwin Upper Marine beds, and which on the Minilya and Lyndon Rivers consist dominantly of dark to carbonaceous sandy shales.

The *Deltopecten subquinguelineatus (comptus)* beds of the Wooramel and Gascoyne rivers must be on about the same geological horizon in the Byro.

It is of general interest to refer to Mr. Chapman's identification of "probable seed-like bodies", collected by the author in carbonaceous shales about 800 feet above the base of the Byro Stage on the Gascoyne, and to the occurrence of fossil wood (small *Dadoxylon*?) on approximately the same horizon near Merlinleigh Homestead. Possibly these may be correlated with the freshwater deposits of the Collieburn and Cardiff coalfields.

The correlation suggested by this discussion is summarised in the table on page 154.

The general succession of the Permo-Carboniferous as described by T. Blatchford and H. W. B. Talbot<sup>(22)</sup> for the Kimberleys is, in ascending order: Glacial beds, Limestone series, Sandstones with occasional thin limestone beds. This sequence suggests that the units of the North-west section from the Lyons Series up to and including part of the Byro Stage at least are represented in the Kimberley area.

#### Cretaceous.

One of the most surprising results of the recent work has been the recognition of Cretaceous rocks covering the area formerly indicated as Jurassic and much of that shown as Permo-Carboniferous on the geological map of Western Australia.

It should be added that Cretaceous rocks are also reported from the lower Murchison River. F. Forman has noted and collected from outcrops of these beds near

## CORRELATION OF PERMO-CARBONIFEROUS OF IRWIN RIVER, WOORAMEL RIVER AND NORTH-WEST BASIN.

| Irwin River.   |   |                       | Wooramel River and North-West Basin. |  |                                    |
|--|---|-----------------------|--------------------------------------|--|------------------------------------|
| Unit.<br>(After Woonough<br>and Somerville.)   | Lithological<br>Characters.                           | Thickness<br>in Feet. | Unit.                                | Lithological Characters.   | Thickness in Feet.                 |
|  |   |                       |                                      |  | Wooramel<br>(After<br>E. A. Rudd), |
|  |   |                       | Wandagee.                            | Shale, shaly sandstone and lime-<br>stone.   | Gascoyne-<br>Muniya.               |
|  |   |                       | Kennedy.                             | Sandstone.   | 1,250-1,800                        |
|  |   |                       |                                      |  | Not<br>present.                    |
|  |   |                       |                                      |  | 800 ?<br>in bore.                  |
|  |   |                       |                                      |  | 500-700                            |
|  |   |                       |                                      |  | (a) 960-1,160                      |
| Upper Marine.  | Grey to carbonaceous<br>shale with erratics.          | 300                   | Byro.                                | (a) Argillaceous sandstone, mud-<br>stone and shale.                                       | (b) 1,200-1,440                    |
|  |   |                       |                                      | (b) Carbonaceous and sandy shale<br>with thin sandstone and lime-<br>stone beds. Erratics. | (c) 10-15                          |
| Coal Measures.   | (a) Shale<br>Seams.                                   | 50                    |                                      | (c) Highly carbonaceous shale at<br>base.  |                                    |
|  | (b) Mainly sandstone.                                 | 200                   | Wooramel.                            | Sandstone.   | 800                                |
| Fossil Cliff Beds.   | Calcareous shales and<br>limestone.                   | 75                    | Callytharra.                         | Flaggy limestone and calcareous<br>shale.  | 130-280                            |
|  |   |                       |                                      |  | 200-460                            |
| Olive shales,<br>Cephalopod beds.<br>Buff Beds.<br>Bull Paddock limestone.<br>Grey limestone.<br>Spheroidal marls. | Shale and mudstone with<br>thin calcareous beds.      | 1,520                 | Lyons.                               | (a) Shale with thin calcareous<br>beds.  | (a) 170-380                        |
| Glacial Beds.<br>Sub-glacial Beds.<br>Basal grits and boulder<br>clays.  | Grits and clays with<br>boulder beds and<br>erratics. | ?                     |                                      | (b) Sandstone, boulder beds and<br>erratics, with some shale.                              | (b) 1,750-2,100                    |

Hamelin Pool (verbal communication), and E. A. Rudd and the writer have collected from outcrops on the lower Wooramel. Assembling all this information, it may be said that not less than 60 per cent. of the area north of the Murchison River and west of the 115th meridian consists of or is underlain at shallow depths by strata of Cretaceous age.

D. Dale Condit and E. A. Rudd recognised<sup>(12)</sup> that the Cretaceous could be divided into (a) a lower series of radiolarian cherts, white and vari-coloured sandy silts and glauconitic sandstones, which they named the Winning Formation (Series); (b) an upper series of limestones, chalks, shales and glauconite sand.

As a result of a study of exposures not previously seen, re-examination by K. Washington Gray and the author of known outcrops, and as a result also of the co-operation of palæontologists, it is possible to give a good general picture of the sequence and distribution of the Cretaceous.

A complete stratigraphical section of the Cretaceous compiled from surface measurements is not available. Probably most of the units comprising the Winning Series are seen in outcrop, but the mesas in which these occur are widely scattered and detailed measurements have not been attempted (see Plate V, Fig. 2).

Only the top 100 to 300 feet of the Cardabia Series have been studied in outcrop. The lower part has been proved by a number of bores, from some of which core samples have been preserved. These have been examined lithologically and palæontologically (see pp. 159-161). Also the surface geology at and adjacent to a number of other bores has been determined and the relationship established between these outcrops and the upper part of the Cardabia Series. It is thus possible to give the Cretaceous sequence with a fair amount of reliability.

The table on p. 156 shows a generalised sequence in the type localities Winning-Cardabia.

#### (i) Winning Series.

The series is named<sup>(12)</sup> after the well known locality (Winning Pool, Winning Station) between Carnarvon and Onslow. The oldest Cretaceous known in the region, it has the widest distribution. Outcrops extend over a distance of nearly 200 miles from Minderoo Station, on the Ashburton River, to the Gascoyne, overlapping both Permo-Carboniferous and Pre-Cambrian.

| Miocene-Eocene.                 |   | Feet.            | Foraminiferal Dense Limestone.   |
|---------------------------------|---|------------------|--|
| Cardabia Series<br>(1070 ft.).  | Near Remarkable Hill, Cardabia Station.   | 85               | Sandy, white to yellow polyzoal limestone with hard yellowish-green bands up to ten feet thick.  |
|                                 |   | 5                | Glauconite sand to sandstone with ammonites and coprolite.   |
|                                 |   | 115              | <i>Inoceramus</i> marls.   |
|                                 |   | 30               | Gypseous green and grey clay shales.   |
|                                 | Maud Landing Bore.                        | 835              | Chalk with spherulitic barytic <sup>1</sup> concretions (two to three inches in diameter).<br>Mainly chalk, with chalky clays and calcareous claystones. |
| Winning Series.<br>(1,100 ft.). | Windalia Hill (A.46).<br>Winning Station. | 1                | Coarse grit.   |
|                                 |   | 3                | White to pink chert.   |
|                                 |   | 55               | White, yellow-pink and brown light chalky silts with small flakes of white mica.   |
|                                 |   | 40               | Yellow, green and buff sandy siltstones.   |
|                                 |   | 10               | Grey shaly rock (in water is slightly sticky and breaks into small pieces, like bole).   |
|                                 | Winning No. 1 Bore.                       | 1+               | Bright yellow sand with ammonites.   |
|                                 |   | 784 <sup>2</sup> | Mainly dark grey to greenish-grey mudstone, with some fine green sands.  |
|                                 |   | 40               | Green shale.   |
|                                 |   | 145              | Grey mudstone.   |
|                                 |   | 20 <sup>3</sup>  | Green shale.   |
|                                 |   | 3 <sup>3</sup>   | Sand.  |
|                                 |   | 1,101+           |  |

<sup>1</sup> Barytes identified by T. Hodge-Smith.<sup>2</sup> Boring in this unit in progress during field work.<sup>3</sup> Commonly seen in outcrop.

The Winning has not been recognised in outcrop for more than a few miles south of the Gascoyne, but has been identified in borings from Woodleigh Station about forty miles easterly from Hamelin Pool. (Geol. Surv. W.A., File No. 140/1902.) The writer has observed quite extensive outcrops of typical Winning beds on Coolwindy Station, long. 116° east, approximately, between the Wooramel and the Gascoyne Rivers, and from conversation with the manager of Wogla Station it seems fairly certain that they extend at least eight to twelve miles east from Wogla Homestead on the Yannarie River. Most of the bores in the coastal region north of the Wooramel penetrated into the Winning Series, the basal sands being one of the most important aquifers of the North-west artesian basin.

#### (a) *Lithology and Thickness.*

A generalised section of the Winning Series is given above. It consists typically of three units (in ascending

order), namely glauconitic sand or sandstone, yellow, green or dark grey gypseous clay shale, alternations of siltstones (usually white, but also commonly pink, yellow or buff in colour) and white, yellow or pink fine grained cherts (Plate V, Fig. 2). Both cherts and siltstones break with a conchoidal fracture. Lithologically the latter closely resemble diatomite; they look chalky, but rarely react with cold hydrochloric acid.

Many mesas show outcrops of the Winning Series from 100 to 150 feet thick, and it is possible that the thickness of the Series could be worked out from surface measurements. The thickness proved by the Pelican Hill (Bibbawarra) Bore (No. 52) is 300 feet, Brickhouse No. 1 Bore (No. 54) 350 feet, Grierson's Tank Bore (No. 38) 450 feet. Identification of the Series in the bores rests upon determinations made by studying the lithology of the samples, and a study of the micro-fauna by F. Chapman and Irene Crespin, there being very good agreement between the two.

Examination of other bore logs indicates that the Series thickens from south to north, the thickness in the Cardabia-Winning area being about 1,100 feet.

#### (b) *Age and General Relationships.*

Except for the abundance of the belemnite *Dimitobelus diptychus* in the green shales of this series, macroscopic fossils are comparatively scarce, and in most instances are too poorly preserved for specific determination. The following are the only genera recognised with certainty by F. W. Whitehouse: *Synclonema*, *Trigonia*, *Thracia*, *Maccoyella* and *Barbatia*. The rocks in the upper part of the sequence are, however, rich in Radiolaria. According to F. Chapman the commonest forms present are: *Lithocyclia exidis*, *Dictyomitra australis* and *Stichocapsa*.

F. W. Whitehouse suggests that the belemnite beds may be regarded tentatively as equivalents of the Tambo Series (Albian) of Queensland. F. Chapman considers that the radiolarian rocks are practically identical with those from Fanny Bay (Darwin) and, therefore, to be placed in the Upper Albian. Mr. Chapman's remarks apply both to specimens which have been collected from widely separated localities and to core samples from the Pelican Hill Bore.

The relationship of the Winning Series to the underlying Permo-Carboniferous has already been discussed.

The upper limit of the Winning Series appears to be fairly well defined in the bores by the change from foraminiferal chalks (Cardabia Series) to darker shaly beds with nodules of pyrites passing downward into radiolarian mudstones, silts and cherts, but no attempt has been made to trace this in the field. The bore correlations suggest that the contact is regular and that there was no intraformational folding.

#### (ii) Cardabia Series.

Exposures of the highest Cretaceous are largely confined to the eastern scarp of the Giralda-Cardabia Range. K. Washington Gray and the writer have named the series after Cardabia Station, where there are many good outcrops. "Cardabia" is a name which appears in a number of places on the map of Western Australia, but is only in general use for the pastoral holding 120 miles to the north of Carnarvon.

The principal exposures in the Hamelin Pool area are also referable to the lower part of the Cardabia Series. This statement is based not only on their lithological features, but on F. Chapman's determination of their Foraminifera.

#### (a) *Lithology and Thickness.*

The section on page 156 gives a generalised statement of the lithology and thickness of the Cardabia Series. Partial sections down to the top of *Inoceramus* marls have been measured at intervals for fifty miles south of Remarkable Hill, the southernmost being at the head of Salt Lake near K.65. Both in outcrop and in bore samples the Cardabia beds are easily recognisable. They consist dominantly of white chalks to chalky mudstones and marls, commonly with abundant fragments of *Inoceramus* shells and Foraminifera. The highest beds vary from hard and soft yellowish-green polyzoal limestone to glauconitic calcareous sandstone. A glauconite sand occurs commonly between these two dominant lithological divisions, which contain abundant ammonites in places (see page 156 for general section).

The *Inoceramus* marls merit special comment. In some places the prismatic fragments of aragonite are so common and extend over such a thickness of sediment that one is tempted to doubt their organic origin (fragments of shell with thicknesses up to 0.8 inch have been collected).

But on close examination all the pieces are seen to have slight curvature and a search is generally rewarded by finding parts of the shell adjacent to the hinge. There is also a tendency for the fragments to occur in nests with many individual pieces inclined to the bedding of the marls. These shells have evidently been worked over to some extent and stratified. Pieces of redistributed *Inoceramus* are also common in some of the higher limestones.

The following is a section of the Cardabia Series, based on examination of samples from the Pelican Hill Bore, between the depths of 250 and 1,105 feet.

*Partial (?) Section of Cardabia Series, Pelican Hill Bore.*

|       |  |
|-------|--|
| 30 +  | Grey chalky claystone.                       |
| 170   | Chalk.                                       |
| 150   | Calcareous greenish-grey claystone.          |
| 440   | White chalk.                                 |
| 65    | White to grey compact chalk and chalky clay. |
| <hr/> |  |
| 855 + |  |
| <hr/> |  |

This bore is eighty miles south from the nearest exposure of the highest Cardabia beds. There is nothing in the driller's terms or in the samples preserved to suggest the presence of the ammonite green sand or the polyzoal limestone. Chapman identifies *Inoceramus* prisms in the whole sequence. As similar remarks apply to the other bores in the lower Gascoyne, it must be concluded that the highest beds either were not deposited there, or were removed in the early Tertiary. The first suggestion is likely to be the correct one.

The bore data suggest that the Cardabia Series maintains a fairly uniform thickness for the greater part of 130 miles from the Gascoyne (Pelican Hill Bore) to Cardabia Station. There is perhaps 200 feet of thickening in that distance, assuming that the uppermost beds were not deposited on the lower Gascoyne.

*(b) Age and Relationships.*

The upper part of the Cardabia Series contains a number of macroscopic fossils, including ammonites, and the series as a whole is rich in Foraminifera. An ammonite green-sand has been observed and collected from near the top



of the series in localities spaced over a distance of fifty miles. Field work and palæontology agree in suggesting that the same horizon is represented from place to place. Immediately above the ammonites in several places is a bed with lamellibranchs, brachiopods and gastropods, most of which, however, are not very well preserved.

The macro-fossils have been determined by F. W. Whitehouse, and the following notes are from information supplied by him after a preliminary examination :

From ammonite greensand : *Eubaculites* aff. *vagina* Forbes, *Parapachydiscus* sp. cf. *compressus* Spath, *Cunnarites kalika* Stoliczka, cf. *Pseudophyllites indra*, *Phylloceras* cf. *forbesianum* (d'Orb), *Schlvettheria* aff. *simplex* Hoepen, *Schlvettheria* aff. *rousseleti* Grossouvre. Several other genera also present.

Beds immediately above greensand : *Ostrea vesicularis* Lamarck, *Cyclothris* cf. *plicatiloides* Stoliczka, *Pleurotomaria* spp. Many other genera also present. Age : Campanian.

F. Chapman and Miss Crespín have examined a large number of specimens from outcrops and borings, and have determined a very large number of micro-fossils. It is impossible to do justice to their work in a summarised account such as this, but it is hoped that details will be published by them at a later date.

For the most part, their determinations suggest that the Santonian-Cenomanian interval is represented in the collections from beds below the ammonite greensand.

Typical Foraminifera from beds which they consider are probably Santonian are :

*Marssonella oxycona* (common), *Spiroplectammina anceps* (c), *Bolivinoides decorata* (c), *Guembelina globulosa*, *Vaginulina strigillata*, *Lenticulina diademata* (c), *Lenticulina gaultina* (c), *Lenticulina macrodiscus* (c), *Frondicularia decheni*, *Globigerina cretacea* (c), *Globotruncana arca*, *Anomalina polyrrhaphes*, *Anomalina rubiginosa* (c). Ostracoda include *Cytherella williamsoniana*, *Clovata*, *Clovata muensteri* and *Bythocypris silicula* var. *minor*. Cretaceous genera restricted to these beds include *Clavulina amorpha* (c), *Bulimina imbricata* (c), *Pleurostomella fusiformis*, *Nodosaria marcki*, *Nodosaria prismatica*, *Nodosaria velascoensis* (c), *Vaginulina trilobata* (c), *Lenticulina discrepans* (c),

*Pullenia quaternaria*, *Anomalina pertusa* (c), and *Cibicides convexus*.

From the marls and chalks they have identified (among other forms) the following :

*Marssonella oxycona* (c), *Guembelina globulosa* (c), *Bolivinoidea decorata* (c), *Globigerina cretacea*, *Globotruncana canaliculata* (c), *Gaudryina gradata*, *Arenobulimina preslii*, *Pleurostomella obtusa*, *Lenticulina circumcidance*, *Lenticulina diademata*, *Lenticulina macrodiscus*, *Frondicularia decheni*, *Frondicularia cordai*, *Globigerina cretacea*, *Globotruncana canaliculata*, *Anomalina polyrraphes* and *Gyroidina nitida*. Cretaceous species restricted to these beds include *Frondicularia* sp. nov., *Lenticulina turgidula* and *Vitriwebbina laevis*. *Spiroplectoides complanata*, *Bolivina incrassata* (c), *Guttulina adhærens* var. *cuspidata*.

As a whole they consider the marls and chalks may be referred to the Turonian Stage of the Upper Cretaceous, and that possibly beds as low as Cenomanian are also present.

It seems likely from these palæontological determinations that a fairly complete sequence of Cretaceous beds may be present in the North-west Basin, as follows :

|                  |  |
|------------------|--|
| Cardabia Series. | Polyzoal limestone.<br>Anmonite greensand .. Campanian.<br><i>Inoceramus</i> marls.<br>Chalks, chalky clays and clay-stones. } Santonian-Turonian. |
| Winning Series.  | Siltstones, cherts, shales and glauconitic sands .. .. Albian.   |

The nature of the Winning-Cardabia contact has already been briefly discussed.

In the northernmost exposures the Cardabia Series passes upward into the Eocene, but near Salt Lake they pass upward into limestones tentatively referred to the Lower to Middle Miocene. The conditions, therefore, are those of overlap, the younger Tertiaries extending furthest south.

The Cretaceous and Tertiary have been folded to much the same extent. Correlations of bores in the coastal M—June 3, 1936.

region bring out very clearly the fact that folds are approximately equally developed from the base of the Cretaceous at least to the Miocene.

### Tertiary and Post-Tertiary.

In the main the area of Tertiary deposition probably approximated that of the Cardabia Series. The maximum development of the beds is in the North-West Cape Range. They consist mainly of limestones, with a total thickness of not less than 700 feet, ranging in age possibly from Upper Oligocene to Mio-Pliocene. On the western side are coral limestones overlaid by cemented sands, with interbedded thin foraminiferal limestones.

The lowest Tertiary beds known are those discovered by Condit and Rudd between Bullara and Giralda.<sup>(12)</sup> Chapman and Crespin refer these beds to the Middle to Upper Eocene.<sup>(23)</sup>

The post-Tertiary deposits include shelly beach deposits, oolitic limestones, sands, travertine or kunkar and coral reef rock of Pleistocene to Recent age. These are found along the coast between Onslow and Cape Locker, and they appear to be warped into very gentle folds parallel to the coast.

Shell-beds are well developed around Salt Lake and along the lower Wooramel River, probably not more than twenty feet above sea-level. Deposits of kunkar ("travertine") cover large expanses, and sandhills are extensive in certain areas. Some of these are fixed by vegetation.

### GEOLOGICAL HISTORY.

There is no record of geological events anywhere in the North-west Basin or in the areas to the south as far as the Irwin River from the time of the great granite intrusives of the Mosquito Series (Pre-Cambrian) until late in the Palæozoic. Upper Palæozoic sedimentation commenced with the deposition of glacials. The erratics in these glacials can all be matched in the Mosquito Series and, moreover, granitic types greatly predominate. Thus if early or middle Palæozoic rocks were ever deposited, they had been completely removed from those parts of the basin which can be examined before the Carboniferous, and the highlands bordering the basin on the east had

been worn down to their granite core for a distance of at least 430 miles bordering the Permo-Carboniferous sea.

Upper Palæozoic sedimentation commenced with the deposition of conglomerates and felspathic sandstones (Lyons Series). These basal sandstones contain pieces of mica up to 0.3 inch across, and have the appearance of typical glacial derivatives, the component pieces of quartz and feldspar being angular and the cement kaolin. It is not likely that deposits of this kind would have been formed far off-shore.

The size and abundance of the boulders (many of them three to four feet in diameter, and well rounded) show derivation from a landscape with considerable relief. There is no evidence to show conclusively in what environment the lowest beds were deposited, but marine fossils are found not very far up in the sequence.

As time went on a great thickness of marine glacial deposits accumulated; the nature of the matrix changed from arkosic sands to fine-grained shaly sandstones and clay shales. Ripple marking and the presence of limestone shows that this change was due rather to basin filling and decreasing relief with offshore deposition than to deepening of the basin.

The cessation of glacial conditions shows climate amelioration, and this factor alone may have been sufficient to allow marine life to flourish.

The change in the lithology of the underlying glacials and the nature of succeeding deposits (sandstone and coal seams) suggests that in Callytharra time topographic relief was low and drainage poor.

The succeeding phase represents a sharp change of conditions. The fact that the Wooramel sandstone, with its sparse marine fauna, rests upon the Callytharra limestone with no shales between suggests that sea regression took place rapidly. The sands were deposited under shallow water marine conditions for the most part, as shown by the presence of cross-bedding and the passage upwards into carbonaceous sediments.

The subsequent record is one of quieter changes. Following Wooramel time, deposition took place at and near sea-level of carbonaceous shales and coal seams. Marine conditions supervened and ice rafts with small erratics again appeared in the sea. For a long period of time a shallow sea persisted and there were no dramatic episodes. Shallow water conditions are proved by the

presence of limestones, ripple marks, worm tracks, grouping of fossils and diversely directed cross-bedding (as shown by the Jimba Jimba sandstones). This chapter closed with a reversion to Wooramel conditions and the deposition of the Kennedy sandstones.

It should be remembered that the area within which the beds below the Kennedy sandstone can be studied represents a long narrow strip trending northerly parallel to the eastern margin of the basin. Except for the little information provided by the Cardabia bores the lithology of these sediments in the deeper parts of the basin is unknown. The bore records show, however, that the Kennedy and Wandagee Beds persist into the deeper parts of the basin with no marked lithological changes, and that the sediments generally are increasingly shaly to the north-west.

After the deposition of the Kennedy sandstones the sea advanced upon the land again, marine life flourished, and a considerable thickness of shales and calcareous beds was built up. Thus closes the record of Palæozoic sedimentation.

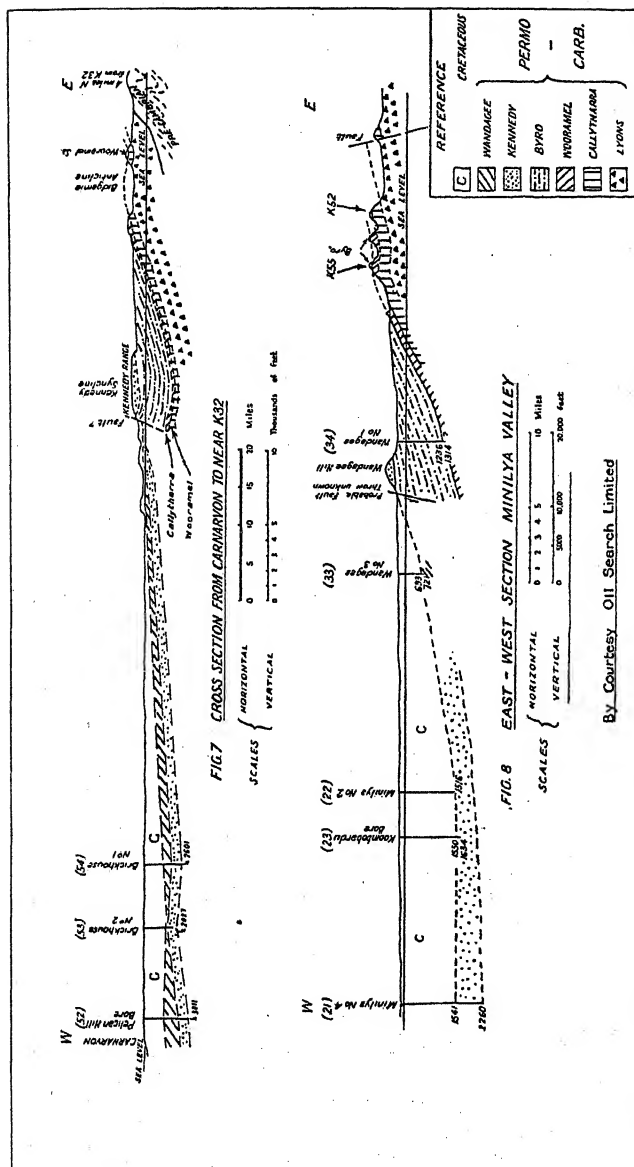
So far as known, the whole of Triassic and Jurassic time is unrepresented in the North-west Basin, but freshwater Jurassic deposits rest upon the Permo-Carboniferous at the Irwin River. In late Palæozoic to Jurassic time folding of the Permo-Carboniferous took place. This folding was probably associated with the rising of the old bordering range, since the folding is sharpest nearest the margin of the basin and more gentle basinwards (see Figs. 7, 8). Unlike the late Palæozoic folding in Eastern Australia, no igneous activity accompanied this diastrophism.

In the Albian epoch the whole region was submerged beneath the sea and much of it remained thus until well into the Tertiary. The sea extended far inland, and Cretaceous sediments were deposited both on the folded Permo-Carboniferous and the basement complex.

From Albian time the record shows an almost unbroken sequence of sedimentation to the present day. In general, the deposits of each successively younger period appear to have been deposited in a sea retreating to the north-west.

In late Tertiary time marked folding again took place, Miocene marine deposits being warped up to 1,200 feet above the sea in the Cape Range region.

Post-Cretaceous faulting has been observed at several places. It is probable that this faulting accompanied the



late Tertiary folding. (The writer agrees with Woolnough and Somerville<sup>(19)</sup> that the Urella fault in the Irwin River district is post-Jurassic.) Certainly it pre-dated extensive erosion, which in its turn was followed by conditions favouring the formation of duricrust (<sup>(24)</sup>, p. 27), now in process of denudation. (See Plate V, Fig. 2).

The fold movement which commenced in the late Tertiary is probably still in progress. The relics of wave-cut terraces at several levels, so beautifully exhibited on the west coast of North-west Cape, are eloquent testimony of the fact that the land has been rising in the recent past, and the sub-recent deposits near Onslow also appear to be gently warped.

One of the latest events has been dune formation. The fact that vegetation is now able to hold these dunes (if not interfered with by excessive stocking) shows that the present climate is better than that of the immediately preceding cycle.

#### STRUCTURE.

As the investigations described in this paper were primarily stratigraphical, observations on structure were more or less incidental. The principal structural lineaments of the area can, however, be given.

The region is structurally part of a basin with late Palæozoic to Recent sediments resting upon a Pre-Cambrian basement and dipping gently westerly to north-westerly. (Figs. 7, 8.) This can be inferred from a glance at the geological map, since rocks of successively younger age are arranged upon each other from east to west. Many reversals of the regional westerly dips have been noted, particularly in the more easterly parts of the region. Folding is more or less general over the whole area of outcrop, and bore correlations show that this condition persists in the areas where outcrops are obscured.

#### Structures in Outcropping Permo-Carboniferous.

A comparatively narrow structurally disturbed area trending about north 15° west persists for 135 miles from the Arthur River almost to the Lyndon near Moogooloo Peak. The structure at the south end is an anticline (Bidgeamia Anticline), the outcropping limbs of which, as defined by the Callytharra limestone, are seven to eight miles apart. (The anticline is bordered on the east by a fairly sharp syncline, the axis of which trends north 15°

west through K.34.) From the Lyons River northward, whilst folds are still in evidence, a number of normal faults make their appearance, the strikes of which are parallel to the axes of folding. Chief of these are the Moogooree faults, which extend at least from near Mt. Sandiman shearing shed to K.51 on the Lyndon River (forty miles). These faults form a series of steps, the amount of throw on the main fault near Moogooree being about 500 feet.

North of Williambury Homestead the structure is much disturbed, and between Williambury and Middalya the Callytharra-Wooramel sequence is repeated several times by gentle folding and strike faulting, giving rise to parallel ridges, such as those at Moogooloo and K.34, trending north  $15^{\circ}$  west. Here also are faults striking north  $75^{\circ}$  west. These appear to be minor faults, but the general offsetting to the west of the beds and structure north of the Lyndon as compared with those south of it suggests that there may be a major fault present trending north  $75^{\circ}$  west and throwing down to the south.

The Kennedy Range is a synclinal and possibly a basin structure. All along the eastern edge the beds have very gentle westerly dips, and along the western edge high ( $30^{\circ}$  to  $55^{\circ}$ ) easterly dips. At the north end the dips have southerly components. Thus a markedly asymmetrical syncline is defined with its axis near the western margin of the range. This structure has had an interesting effect on water supply. The Kennedy sandstone rests on clay shales at the top of the Byro, and where this contact reaches the surface along the western side of the syncline springs issue, yielding water suitable for use by stock. A normal strike fault is also present here, involving both Permo-Carboniferous and Cretaceous (see below, and p. 109).

Gentle folding and minor faulting are characteristic of the Permo-Carboniferous along the Minilya River on Middalya and Wandagee Stations.

#### Structures in Cretaceous and Tertiary.

*Folds.*—A number of folds, several of them domes, have been observed in the Cretaceous and Tertiary. In all those examined the rocks of both systems are folded to much the same extent and bore correlations show the same relationship.

All these structures strike north  $10^{\circ}$  east to north  $25^{\circ}$  east. Principal interest attaches to the anticlines: Cape Range, Rough Range and Giralia Range. All except the



Giralia fold are expressed topographically as ridges curved in section. The eastern flank of the Giralia anticline is much modified by erosion.

*The Cape Range Anticline* forms almost the whole of the peninsula after which it is named. At sea-level it is 100 miles in length and 25 miles in width. Its topographic relief is not less than 1,200 feet, and this is likely to be an approximate measure of the amount of closure on the structure. The eastern limb dips at from six to eight degrees. Dips of two degrees were noted on the western limb. Erosion of this structure exposes beds from Miocene to Lower Miocene in age. Folding on Cape Range was first noted by F. G. Clapp.<sup>(7)</sup> W. G. Woolnough observed some interesting details in the structure of the range during his air reconnaissance.<sup>(10)</sup>

*The Rough Range Anticline* borders the southern end of the Cape Range anticline, to which it is parallel. At sea-level the anticline is twenty-three miles in length and from one to three miles in width. The maximum amount of topographic relief is 350 feet. The few observations made on this structure suggest that, like the Cape Range, the eastern limb has a steeper dip than the western. Dips up to 8° were noted on the east flank and perhaps 1° to 2° on the west. All the beds exposed are probably Upper Miocene to Sub-Recent. The structure appears to be one of those noted from the air by W. G. Woolnough in 1922.<sup>(10)</sup>

*The Giralia Anticline*, discovered by Clapp, extends from near the mouth of the Lyndon River to the head of Exmouth Gulf (sixty-five miles). Near Giralia both flanks are clearly defined. The dips are low (not more than 3°), the eastern limb perhaps having the steeper dip. The Tertiary and Cretaceous are exposed on this anticline. Almost all the Tertiary beds have been removed from the eastern limb, where erosion has proceeded down to the Winning Series.

Other structures have been noted, but information concerning them is regarded as confidential at present.

#### Faults.

Evidence of faulting in Cretaceous beds (Winning Series) has been observed in three localities. Near Cahill's Outcamp the Cretaceous dip to the east-north-east at 70° and on the Minilya River three miles below Coolkilya Pool they strike north 10° west and stand vertically. All the beds, Cretaceous and Permo-Carboniferous, hereabouts are much disturbed.

Seven miles south-westerly from K.54 a fault (Middalya Fault) involving both Permo-Carboniferous (Kennedy sandstone) and the Winning Beds, is exposed. This has been figured and described in an earlier part of this paper (see Fig. 1 (b)).

It will be observed that the strike of these faults is approximately the same as those in the Permo-Carboniferous.

#### Age of Folding and Faulting.

It has been shown already that the Permo-Carboniferous was folded prior to the deposition of the Cretaceous (pp. 108-109). If the folding of the Permo-Carboniferous in the North-west and Irwin River areas was synchronous, it certainly took place before the Jurassic period, and was thus of late Palaeozoic or Triassic age. The most reasonable assumption is that this folding occurred in the late Palaeozoic.

There is indubitable evidence also that there was no marked structural deformation during most of Cretaceous and early Tertiary time, and that folding took place on a large scale in the late Miocene or Pliocene. This folding was of sufficient magnitude to warp upwards marine Tertiary deposits to a height of 1,200 feet on the Cape Range anticline.

Faults in the Permo-Carboniferous and Cretaceous have been briefly described. Some of these are certainly post-Cretaceous, and may be of the same age as the Urella fault near Mingenew, which is post-Jurassic.

The relationship of the strike of the faults and the fold axes in the Permo-Carboniferous is consistent with an interpretation that they relate to the same diastrophism, but one is faced with the fact that the faults definitely of post-Cretaceous age have a similar strike.

As described above, there is a noteworthy divergence between the strikes of the folds in the Permo-Carboniferous and the younger sediments. This apparent divergence, however, is probably misleading, since the two areas are differently situated. In all probability the fold axes of the Permo-Carboniferous to the north of their area of outcrop curve round parallel to those in the younger sediments near the coast.

The bore correlations, however, suggest that in the deeper parts of the basin the Cretaceous was deposited upon a gently warped basement of Permo-Carboniferous, and

that both were involved in subsequent folding, the old warps in the basement perhaps controlling the locus of the younger folds.

The history of sedimentation in the region shows that there have been two periods of loading in the basin, the Permo-Carboniferous and the Cretaceous-Tertiary, and it is reasonable to suppose that each period of sedimentation ended with crustal activity, giving rise to folds and faults. A simple and adequate explanation of the structures in the region is that, following each period of sedimentation, the basin filling was subject to compression from the ocean towards the land, the sediments being wrapped about the old (Pre-Cambrian) massif, giving rise to structures oriented parallel to it. The orientation and position of the younger folds was largely determined by those of the older.

#### Structural Control of Topography.

A knowledge of these structures throws a good deal of light on the topography of the coastal region. Thus Exmouth Gulf probably represents a syncline between the Cape Range and Giralda anticlinal axes, an extension of the trough to the south being marked by the Post-Tertiary deposits of Cadabia and Waroora. K. Washington Gray's discovery of Tertiary sediments at Cape Cuvier and Red Bluff rising seawards, taken together with the fact that the structural lines of the region curve in sympathy with the exposed western margin of the basement, suggests a continuation of the Cape Range or a related anticlinal axis southerly to that area.

The north end of Salt Lake occupies a syncline and the main body of the lake occupies either a syncline or an area of local dip flattening bordering the easterly-dipping beds which form the barrier between Salt Lake and the sea.

Clearly the trend of some of the streams is structurally controlled. The parallelism of the main watercourses, Wooramel, Gascoyne, Minilya and Lyndon, suggests structural control. The bore correlations prove beyond question that this control is not east-west faulting. These streams probably originated on a Cretaceous-Tertiary surface dipping gently westward.

#### ARTESIAN AND SUB-ARTESIAN BORES.

About eighty bores, ranging in depth from 570 to 4,013 feet, have been put down in the coastal strip extending from Onslow to the Wooramel River. Most of these have

been put down along the lower portions of the Wooramel, Gascoyne, Minilya and Lyndon Rivers.

The bores are indicated by numbered circles on the maps, and a reference list is given herewith.

**List of Bores.**  
(Lower Gascoyne and Northwards.)

| No. on Map. | Name.                                       | Depth.    |               |
|-------------|---|-----------|---------------|
| 1           | Onslow.                                     | 1,728'    | Artesian.     |
| 2           | Cardabia Centenary.                         | 2,436' 2" | Artesian.     |
| 3           | Cardabia Maud Landing or "Govt. Bore".      | 2,359'    | Artesian.     |
| 4           | Cardabia No. 2 or Tarrawarra.               | 2,506'    | Sub-artesian. |
| 5           | Cardabia No. 1.                             | 4,013'    | Sub-artesian. |
| 6           | Winning No. 1 or "12 Mile".                 | 1,043'    | Sub-artesian. |
| 7           | Winning No. 2.                              | 2,009'    | Sub-artesian. |
| 8           | Mia Mia No. 6.                              | 1,320'    | Sub-artesian. |
| 9           | Mia Mia No. 3 Sub-Artesian (Station No. 2). | 698'      | Sub-artesian. |
| 10          | Mia Mia No. 2.                              | 1,320'    | Artesian.     |
| 11          | Mia Mia No. 3.                              | 693'      | Sub-artesian. |
| 12          | Mia Mia No. 1 or Four Corners.              | 1,217'    | Sub-artesian. |
| 13          | Mia Mia Old No. 1.                          | —         | Artesian.     |
| 14          | Mia Mia No. 5.                              | 1,281'    | Sub-artesian. |
| 15          | Mia Mia Five Mile or Jam Thicket.           | 2,591'    | Artesian.     |
| 16          | Mia Mia No. 4 or Bumbarry.                  | 1,197' 6" | Artesian.     |
| 17          | Mia Mia No. 1 East or Pleiades.             | 392' 8"   | Sub-artesian. |
| 18          | Mia Mia No. 2 East or Pleiades No. 2.       | 838'      | Sub-artesian. |
| 19          | Warcoora No. 1.                             | 1,774'    | Artesian.     |
| 20          | Minilya "C", Korilling or Old No. 4.        | 1,694'    | Artesian.     |
| 21          | Minilya No. 4 or Gerardi.                   | 2,260'    | Artesian.     |
| 22          | Minilya No. 2 or Koomoonoo.                 | 1,516'    | Artesian.     |
| 23          | Minilya, Koombobardu.                       | 1,634'    | Artesian.     |
| 24          | Minilya No. 3 or Chirrita.                  | 2,255'    | Artesian.     |
| 25          | Minilya "B" or Gnabyarra.                   | 1,408'    | Artesian.     |
| 26          | Minilya No. 1 } Neemarabardu                | 1,208'    | Artesian.     |
| 27          | Minilya "A" } Bores.                        | 1,000'    | Artesian.     |
| 28          | Minilya No. 6 or Booloogooroo Boundary.     | 1,315'    | Artesian.     |
| 29          | Minilya No. 5 or Coolan.                    | 1,698'    | Artesian.     |
| 30          | Wandagee No. 4 or Minilya Brighton.         | 736'      | Sub-artesian. |
| 31          | Wandagee No. 5.                             | 441'      | Sub-artesian. |
| 32          | Wandagee No. 6.                             | 1,050'    | Sub-artesian. |

## (Lower Gascoyne and Northwards—Continued.)

| No. on Map. | Name.                          | Depth.    |               |
|-------------|--------------------------------|-----------|---------------|
| 33          | Wandagee No. 3.                | 721'      | Sub-artesian. |
| 34          | Wandagee No. 1.                | 1,314' 6" | Sub-artesian. |
| 35          | Wandagee No. 2.                | 1,345'    | Sub-artesian. |
| 36          | Yalobia No. 1.                 | 1,008'    | Artesian.     |
| 37          | Manberry, No. 1.               | 1,356'    | Artesian.     |
| 38          | Booloogooroo, Grierson's Tank. | 1,510'    | Artesian.     |
| 39          | Booloogooroo No. 1.            | 1,664'    | Artesian.     |
| 40          | Boolathanna No. 8.             | 1,604'    | Artesian.     |
| 41          | Boolathanna No. 10.            | 1,253'    | Artesian.     |
| 42          | Boolathanna No. 9.             | 1,508'    | Artesian.     |
| 43          | Boolathanna No. 11.            | 1,666'    | Artesian.     |
| 44          | Boolathanna No. 3.             | 1,461'    | Artesian.     |
| 45          | Boolathanna No. 12.            | 1,683'    | Artesian.     |
| 46          | Boolathanna No. 1.             | 1,650'    | Artesian.     |
| 47          | Boolathanna No. 6.             | 3,400'    | Artesian.     |
| 48          | Boolathanna No. 2.             | 1,392'    | Artesian.     |
| 49          | Boolathanna No. 5.             | 1,506'    | Artesian.     |
| 50          | Boolathanna No. 4.             | 2,834'    | Artesian.     |
| 51          | Boolathanna No. 7.             | 1,650'    | Sub-artesian. |
| 52          | Pelican Hill or Bibbawarra.    | 3,011'    | Artesian.     |
| 53          | Brickhouse No. 2.              | 2,027'    | Artesian.     |
| 54          | Brickhouse No. 1.              | 2,634'    | Artesian.     |
| 55          | Brickhouse No. 3.              | 1,813'    | Artesian.     |
| 56          | Brickhouse No. 6.              | 1,920'    | Artesian.     |
| 57          | Brickhouse No. 4.              | 1,460'    | Artesian.     |
|             | Brickhouse No. 5.              | —         | —             |
| 59          | Callagiddy No. 2.              | 1,922'    | Artesian.     |
| 60          | Callagiddy No. 3.              | 1,583'    | Artesian.     |
| 61          | Callagiddy No. 1.              | 1,244'    | Sub-artesian. |

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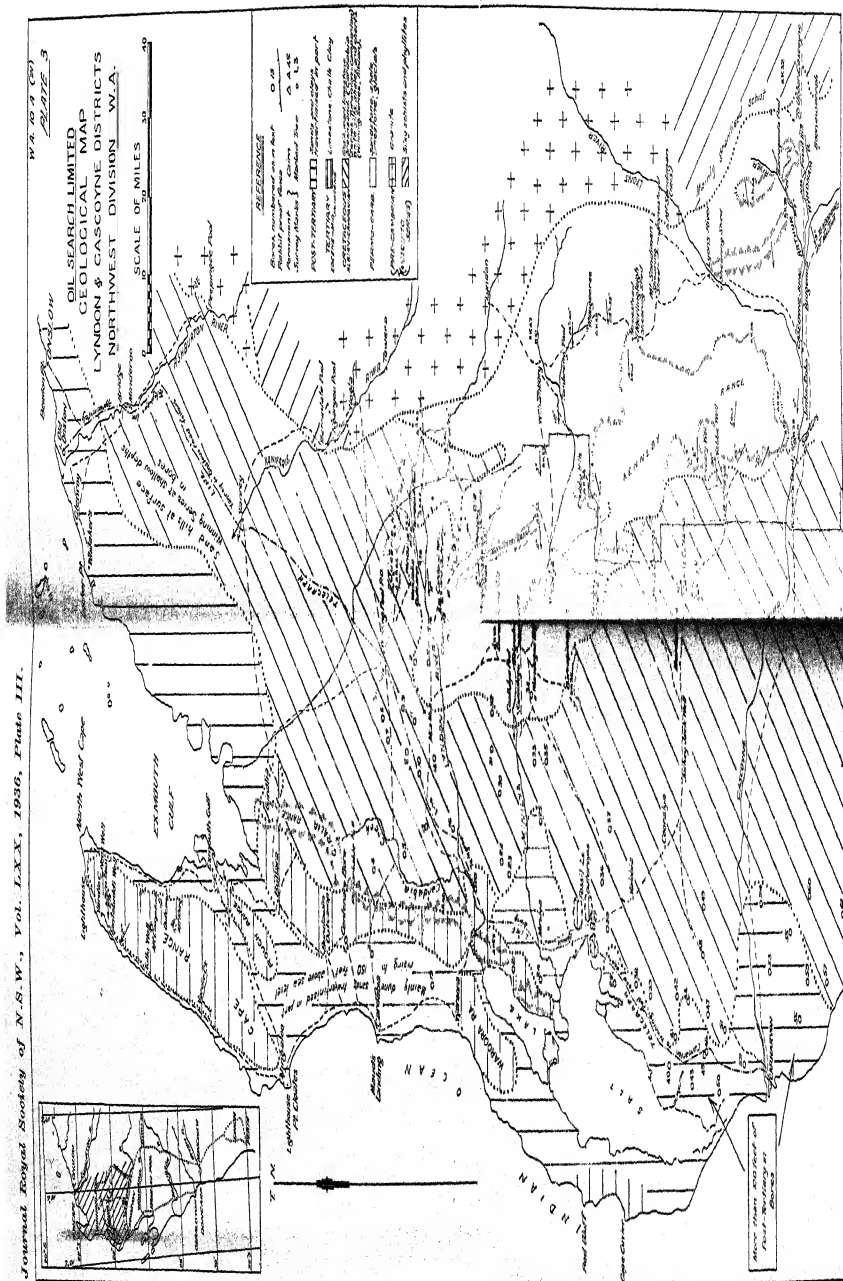
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### EXPLANATION OF PLATES.

III. Geological map of Lyndon and Gascoyne Districts, North-West Division, Western Australia.

IV. Map showing distribution of Permo-Carboniferous units, North-West Division, Western Australia.



**OIL SEARCH LIMITED**  
**MAP**  
**SHOWING IN DETAIL**  
**AREA OCCUPIED BY**  
**PERMO-CARBONIFEROUS**  
**N.W. DIVISION**  
**WESTERN AUSTRALIA**

**RECEIVED**

[illegible]

W. L. G. G.







Fig. 1.



Fig. 2.



CYANOGENETIC GLUCOSIDES IN AUSTRALIAN  
PLANTS.PART 4.—*ZIERIA LAEVIGATA*.

By H. FINNEMORE, B.Sc. (Lond.), F.I.C.,  
and (MISS) JOYCE M. COOPER, B.Sc. (Syd.).

(Manuscript received, May 25, 1936. Read, June 3, 1936.)

*Zieria laevigata* Sm. (Rutaceae) is a glabrous erect shrub, from one to two feet high, distributed throughout the sandstone country of New South Wales, Queensland, and Victoria. In New South Wales it occurs from the coastal districts to the tablelands. The specimens examined were collected in French's Forest, in parts of which it grows in some profusion. Both this plant and *Z. Smithii* were found to be cyanogenetic by Petrie in 1912,<sup>(1)</sup> but so far as we are aware no losses of stock have been traced to them. On the other hand we have been informed by Mr. W. L. Hindmarsh, Director of the Veterinary Research Station at Glenfield, that *Z. Smithii* has been suspected of poisonous properties quite unconnected with any hydrocyanic acid it may evolve, and that the variety *Z. laxiflora* was thought to be responsible for fatalities in 1931.

Apart from any direct implication, it seemed desirable to take the opportunity of studying the amount of hydrocyanic acid evolved from the plant under different conditions and also of determining the constitution of the cyanogenetic substance which is present, especially in view of the fact that so few of these are known. It is shown in the present paper that the hydrocyanic acid is combined on the one hand with glucose and on the other with meta-hydroxybenzaldehyde. It is thus very nearly related to dhurrin, the glucoside of sorghum and sudan grass, which is a similar derivative of para-hydroxybenzaldehyde. Neither meta-hydroxybenzaldehyde nor its derivatives seem to have been previously observed in nature, although salinigrin, the glucoside of one of the willows, *Salix nigra*, was formerly thought by Jowett<sup>(3)</sup> to be derived from this substance, but this has been since

shown by him not to be the case. It is of interest to compare the rate of hydrolysis of the glucoside now obtained, to which the name *zierin* has been given, with that of *dhurrin*. The latter was found by Dunstan and Henry<sup>(2)</sup> to be completely decomposed by heating for five minutes on the water bath with hydrochloric acid of about one per cent strength. Under the same conditions less than seven per cent of *zierin* is decomposed.

#### EXPERIMENTAL.

This work was begun some seven years ago with Miss S. K. Reichard, B.Sc., when a small quantity of the pure glucoside was obtained by the fractional precipitation of the acetone extract with benzene. The work was resumed in August last, when material in the late flowering stage was collected. The identity of the plant was confirmed for us by Mr. Edwin Cheel, Government Botanist, to whom our thanks are due. On steam distillation of 100 grammes a small quantity (0.2 g.) of a viscous, golden-yellow, unpleasant-smelling oil was obtained. It seemed possible that the oil might contain the cyanhydrin or the ultimate constituent of the break-down of the glucoside, for when such a plant is distilled a certain amount of enzyme action may occur before the steam has raised the temperature of the plant material to that at which the enzyme becomes inactive. Particularly did this seem possible because microscopic examination revealed no signs of oil glands or secreting hairs. It was seen later that there is no connection between the volatile oil and the cyanogenetic glucoside, as in the first instance meta-hydroxybenzaldehyde was not volatile in steam, nor did the volatile oil contain nitrogen, as would have been the case had some of the cyanhydrin been present.

#### Determination of the Hydrocyanic Acid Evolved

All the aerial parts of the plant, including the flowers and fruit, contain both enzyme and glucoside, and when crushed evolve hydrocyanic acid. There was a loss of about 25 per cent when the plant was stored for six years. The respective amounts of hydrocyanic acid yielded by the action of its own enzyme and when excess of enzyme from sweet almonds is added were determined by the method previously described in this journal,<sup>(4)</sup> modified on account of the interference of the volatile oil which distilled with

the hydrocyanic acid. The alkaline cyanide solution was steam distilled for one hour before proceeding with the iodine titration in the usual way. The figures in the following table show that with its own enzyme approximately half of the glucoside present is decomposed. Seasonal variation seems to be slight, as shown by the figures obtained in May, June, and August. The results are also given for the silver nitrate method of estimation, the end point of which was not sharp. The plant comes into the category of potentially poisonous ones, containing as it does about ten times the limiting amount fixed by Seddon and King<sup>(5)</sup> for this class.

AMOUNT OF HYDROCYANIC ACID FROM *ZIERIA LAEVIGATA*.

| Ref. No. | Date of Collection.           | Percentage of HCN<br>Calculated on Material<br>Dried at 100° C. |                                  |
|----------|-------------------------------|---|----------------------------------|
|          |                               | (1) Iodine<br>Method.   | (2) AgNO <sub>3</sub><br>Method. |
| 1256     | August, 1929.                 | 0.46  |                                  |
|          | Redetermined 1936.            | 0.34  | 0.39                             |
| 3397     | August, 1935.                 | 0.40  | 0.45                             |
| 3433     | April, 1936.                  | 0.49  |                                  |
|          | (With its own enzyme<br>only) | 0.20  |                                  |
| 3454     | June, 1936                    | 0.39  |                                  |
|          | (With its own enzyme)         | 0.16  |                                  |

#### Extraction of the Glucoside.

A preliminary experiment was made by treating 100 grammes of the coarsely powdered flowering tops with acetone in a Soxhlet apparatus for eight hours, when 87 per cent of the total amount of glucoside was extracted. Much plant wax was removed at the same time. Experiments were therefore made with the following solvents at the ordinary temperature: acetone, alcohol, and a mixture of equal parts of these. Although acetone removed only 43 per cent of the glucoside, as against 80 per cent by the other solvents in the same time, it was preferable to use this because of its limited solvent action

N—June 3, 1936.

on other plant constituents. About six kilos. of material were extracted by percolation with cold acetone. The total amount of glucoside removed was found, by analysis of the extract, to be about 60 per cent. The complete extraction was then effected by cold alcohol, but it was impossible to obtain the glucoside in crystalline form from this alcoholic extract.

#### The Acetone Extract.

After removal of the acetone the deep green syrupy residue was repeatedly washed with petroleum ether to remove fixed oils. It was then refluxed with ethyl acetate and the solvent removed. The ethyl acetate extract was then concentrated under reduced pressure and dissolved in ethyl acetate, previously dried over potassium carbonate. Crystals of the glucoside in an almost pure condition were thus obtained. An alternative method, which gave a fairly good yield, was to dissolve the first ethyl acetate extract in acetone and fractionally precipitate with benzene. The first fractions were syrupy, and showed no tendency to crystallise. The third and fourth rapidly crystallised, and finally detached crystals separated in the acetone-benzene mixture.

#### Purification of the Glucoside.

It was extremely difficult to remove the last traces of adhering syrup from the crystals of the glucoside; washing with cold ethyl acetate removed some of the syrup, but solution in hot acetone and the addition of benzene caused the separation of a small amount of flocculent material, and the addition of more benzene gave a yield of fairly pure glucoside in tufts of small flattened needles. Methyl ethyl ketone can with advantage be substituted for acetone. At a later stage of the purification the glucoside was dissolved in hot ethyl acetate, and a small quantity of chloroform added to this caused the rapid separation of the pure glucoside.

The glucoside, which it is proposed to designate zierin, is extremely soluble in water, alcohol, acetone and methyl ethyl ketone, but almost insoluble in chloroform, ether, petroleum ether, or benzene. It softens at 153° C., and melts completely at 156° C. The aqueous solution gives a faint purplish-blue colour with ferric chloride. It is distinguished from the glucosides derived from benzal-

dehyde cyanhydrin by the absence of a red colour when mixed with a little sulphuric acid. It is lævo-rotatory,  $[\alpha]_D^{20.2} = -29.5$ . When dried at  $105^\circ$  for four hours it showed no loss of weight.

On analysis,<sup>1</sup>

|  |      |        |                 |     |        |                     |        |        |
|--|------|--------|-----------------|-----|--------|---------------------|--------|--------|
| 0.1222   | gave | 0.2462 | CO <sub>2</sub> | and | 0.0652 | H <sub>2</sub> O=C, | 54.95, | H=5.93 |
| 0.1006   | "    | 0.2013 | "               | "   | 0.0520 | "                   | 54.57  | 5.74   |
| 0.1394   | "    | 0.2762 | "               | "   | 0.0706 | "                   | 54.04  | 5.63   |
| C <sub>14</sub> H <sub>17</sub> O <sub>7</sub> N requires C=54.0, H=5.5. |      |        |                 |     |        |                     |        |        |

#### Acetylation of the Glucoside.

About one gramme of glucoside and the same quantity of fused sodium acetate were refluxed with acetic anhydride for one hour. After removing the excess of reagent the residue was washed with water and recrystallised from dilute alcohol; rhomboidal crystals were obtained, melting at  $115^\circ$  to  $118^\circ$  C. Analysis agrees with either a pentacetyl or a tetracetyl derivative. The solution in alcohol gave no colouration with ferric chloride.

0.1032 gave 0.2078 CO<sub>2</sub> and 0.0494 of H<sub>2</sub>O, C=54.92, H=5.32.

C<sub>14</sub>H<sub>13</sub>O<sub>7</sub>N(CH<sub>3</sub>CO)<sub>4</sub> requires C=54.8, H=5.2.

#### Hydrolysis of the Glucoside.

The glucoside was hydrolysed both with almonds and with emulsin by the method used in the determination of hydrocyanic acid in plants; the mean of three estimations was 8.6 per cent of hydrocyanic acid, which is in agreement with the above formula. In order to isolate the products of hydrolysis, one gramme of zierin was dissolved in 200 millilitres of water and incubated for two hours at  $43^\circ$  C. with emulsin prepared from almonds. After standing all night the liquid was again incubated for four hours to ensure complete hydrolysis. The aqueous liquid was then steam distilled to remove the hydrocyanic acid which had been formed, filtered from the insoluble protein, and evaporated under reduced pressure to a small bulk. It was then extracted by repeated shakings with ether. When the ether solution was dried and distilled, a yellow syrup was left which soon crystallised. It was then recrystallised from carbon tetrachloride, in which it is

<sup>1</sup> We are indebted to Miss Dorothy K. Large, B.Sc., for these and the following analyses.



sparingly soluble at ordinary temperature. It was thus obtained in flat plates melting at  $103^{\circ}$  to  $104^{\circ}$  C. The yield of the unpurified material from the ether solution was 0.33 g.

#### Identification of the Products of Hydrolysis.

This substance was sparingly soluble in cold, but more soluble in hot water, the aqueous solution giving with ferric chloride a purplish-blue colour indistinguishable from that given by the glucoside. It dissolves in solution of sodium hydroxide with a yellow colouration. With phenyl hydrazine and with *p*-nitrophenyl hydrazine crystalline derivatives were readily obtained. Other reagents were tried, and from the following table it will be seen that the melting points of the derivatives obtained agree with those of meta-hydroxybenzaldehyde, which were prepared for direct comparison, and for the determination of their mixed melting points.

Analysis gave the following:

0.1084 gave 0.2754  $\text{CO}_2$  and 0.0508  $\text{H}_2\text{O}$ , C=69.2, H=5.2  
 0.1108 " 0.2798 " " 0.0512 " " 68.89 " 5.2  
 $\text{C}_7\text{H}_6\text{O}_2$  requires C=68.85, H=4.92.

#### MELTING POINTS OF DERIVATIVES.

|  | Meta-hydroxy-benzaldehyde. | Product from Zierin.   |
|--|----------------------------|------------------------|
|  | C. $^{\circ}$              | C. $^{\circ}$          |
| Hydrazone .. .. .                        | 203-205                    | 204-205                |
| Phenyl-hydrazone .. .. .                 | 138.5                      | 138-139 <sup>(6)</sup> |
| <i>p</i> -Nitro-phenyl-hydrazone .. .. . | 216                        | 216-217                |
| 2.4-dinitro-phenyl-hydrazone .. .. .     | 257                        | 257                    |
| Semicarbazone .. .. .                    | 193                        | 191-192 <sup>(7)</sup> |

Clemm<sup>(6)</sup> gives  $130^{\circ}$ . Borsche and Bolser<sup>(7)</sup> give  $198^{\circ}$ .

In order to prepare a further quantity of the products of hydrolysis, uncrystallisable syrups containing glucoside were dissolved in water and hydrolysed by means of crushed sweet almonds. After filtering off the almond meal the clear solution was extracted with petroleum ether to remove any trace of fixed oil. Half of this was

shaken with ether, which extracted a greenish-yellow oil smelling strongly of hydrocyanic acid and obviously containing the cyanhydrin. A quantitative determination of the hydrocyanic acid evolved on steam distillation showed that the proportion of cyanhydrin present was about 50 per cent. The residue in the distilling flask was extracted with ether, whereupon impure crystals of meta-hydroxybenzaldehyde were obtained. The other half of the hydrolytic product was steam distilled in order to decompose the cyanhydrin and was then extracted with ether, when the meta-hydroxybenzaldehyde was readily obtained.

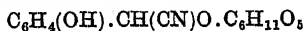
#### The Sugar.

After extracting the hydroxyaldehyde as described above, the liquid was freed from ether and was further evaporated. It readily yielded an osazone, which after recrystallisation from diluted pyridine or from hot water had the characteristic appearance of glucosazone and melted at  $206^{\circ}\text{C}$ . As the solution of the sugar was dextro-rotatory, there can be little doubt the constitution of zierin is represented as the glucoside of the cyanhydrin of meta-hydroxybenzaldehyde.

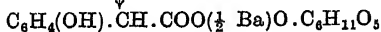
#### Alkaline Hydrolysis of Zierin.

About one gramme of zierin (i) was refluxed with excess of a saturated solution of barium hydroxide. Ammonia was given off slowly for many hours. When this had ceased the excess of barium hydroxide was removed by means of carbon dioxide and the barium carbonate filtered off. The filtrate exerted no reducing action on Fehling's solution. It was then evaporated to a small bulk, first on the water bath and then in a vacuum desiccator. A cream-coloured solid residue was obtained which showed no tendency to crystallise. The barium salt (ii) was then decomposed by the addition of sulphuric acid to its solution in water until acid to congo red, and the barium sulphate then removed by filtration. The solution of the acid gave a clear yellow syrup on evaporation, and after boiling with dilute hydrochloric acid now readily reduced Fehling's solution. The osazone had the characteristic appearance of glucosazone, but was not further examined.

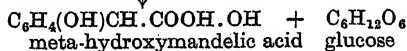
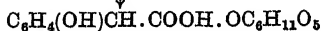
The following scheme shows the probable course of these reactions.



(i) Zierin



(ii) barium salt



meta-hydroxymandelic acid      glucose

#### THE ENZYME.

The ground material which had been thoroughly extracted with acetone was now extracted with water saturated with chloroform. The aqueous extract was added to about three times its volume of alcohol, and the resulting precipitate collected, washed and dried. When it was redissolved in water it was found to hydrolyse zierin, prunasin, sambunigrin rapidly, but its action on amygdalin was slow.

#### SUMMARY.

*Zieria laevigata* yields approximately 0.4 per cent of hydrocyanic acid. This is present in the form of the glucoside of the cyanhydrin of meta-hydroxybenzaldehyde.

#### ACKNOWLEDGMENTS.

Acknowledgments are gratefully made to the University of Sydney for a Science Research Scholarship which has enabled one of us (J.M.C.) to take part in this work, to Professor J. C. Earl, of the Department of Organic Chemistry, for facilities for the combustion of the substances analysed, to Mr. J. T. Tippet for the determinations of the hydrocyanic acid involved in quantitatively following the glucoside through the various stages of its isolation.

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# THE UPPER PALÆOZOIC ROCKS AROUND YESSABAH, NEAR KEMPSEY, NEW SOUTH WALES.

By A. H. VOISEY, M.Sc.

(With Plate VI and five text-figures.)

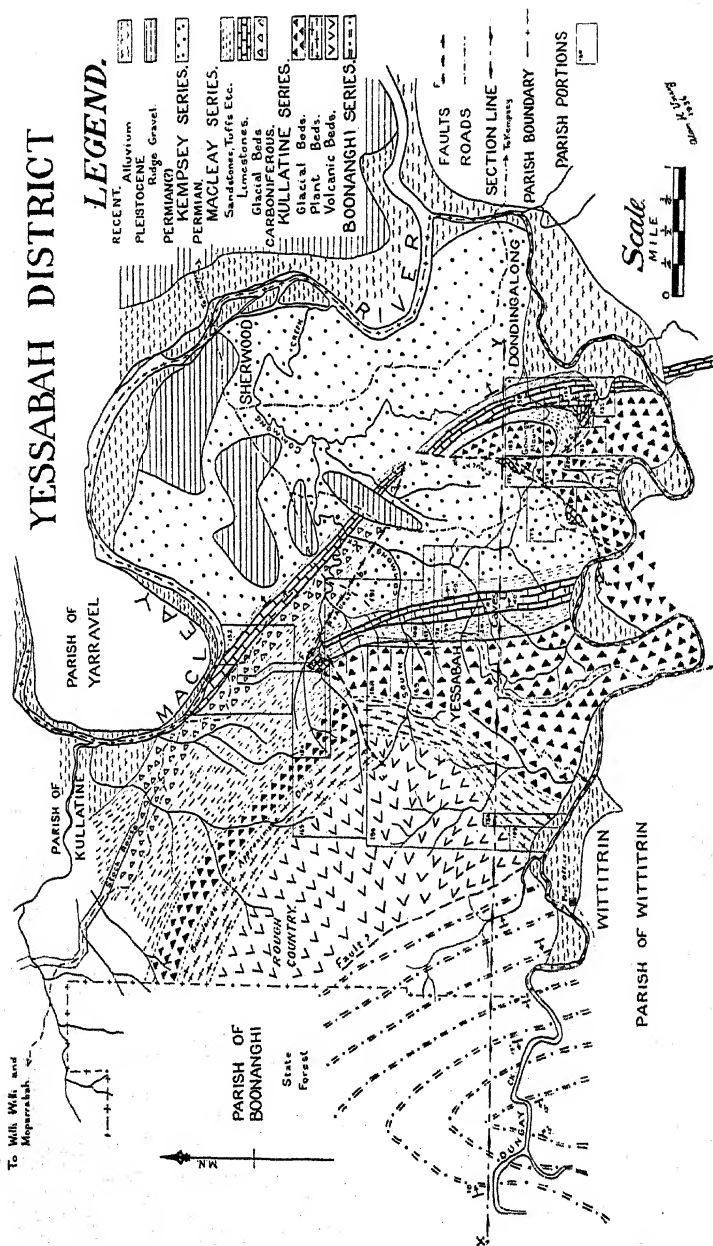
(Manuscript received, March 12, 1936. Read, June 3, 1936.)

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## INTRODUCTION.

This paper deals with the Upper Palæozoic rocks which outcrop in the parish of Kullatine, County of Dudley, around the Yessabah Caves Reserve. The caves are about eleven miles east of Kempsey, which is 313 miles by rail north of Sydney.

Little mention of this area had been made in literature until 1934, when the writer described the main features in a paper entitled "A Preliminary Account of the Geology of the Middle North Coast District of N.S.W.".<sup>(8)</sup> The history of previous geological investigations in the Macleay District was outlined and recognition given to the work of Dr. W. G. Woolnough, who, in 1911, went rapidly through the Willi Willi District, describing some of the beds in the northern portion of the parish of Kullatine. No other information relating to the rocks in the Yessabah region has been found.



The discovery by the writer of *Aneimites* (?) and *Rhacopteris* in chert pebbles among the Permian marine fossils in a branch of Commonong Creek near Yessabah was the first indication of the presence of Carboniferous strata. The fossils were later found *in situ* near the head of this creek.

The possibility of shedding further light upon the Carboniferous-Permian junction led to concentration upon the rocks in the vicinity of Yessabah and, later, Dondingalong. By careful mapping it was hoped that details of the succession of beds would be obtained. This was the case, but structures were found to be so complicated and outcrops so scarce that the task was a difficult one. Boundaries were mapped as well as possible, but the interpretations are offered for criticism.

Most of the difficulties have been caused by the Tait's Creek glacial beds, which are well developed north and north-west of Yessabah, but make few outcrops, and although their presence has been inferred at times, they have not been found in other places, and a certain amount of doubt remains with regard to their whereabouts. Although they are looked upon as the equivalents of the Lochinvar Shales, portions of them are difficult to separate from the underlying Kuttung beds. The calcareous nature of the material and the presence of marine fossils have assisted in the separation. The purple colour is the main criterion, but as some of the Kuttung beds weather similarly, it cannot be relied upon.

## STRATIGRAPHY.

### Lower Carboniferous: The Boonanghi Series.

(See specimens Australian Museum Collection DR 3129 to DR 3165.)

The Boonanghi Series<sup>(8)</sup> occupies the south-western corner of the parish of Kullatine, and consists chiefly of water-sorted felspathic tuffs, bluish-grey sandstones, greenish-grey mudstones, dark grey shales and occasional bands of conglomerate.

The felspathic tuff is the most distinctive and also the most common rock type, and is confined to this series. It is composed of feldspar crystals and chloritic material, but contains very little quartz. The fossils, which are abundant everywhere in this rock, are composed of crystalline calcite. Forms which have been identified are crinoid ossicles, Fenestellidæ, *Loxonema*, *Rhipidomella*, a small

gasteropod, and small lamellibranchs. Further collecting should reveal a greater variety, but most of the remains are fragmental and difficult to identify. The crinoid ossicles are so numerous in the rock that it may be described as a crinoidal felspathic tuff.

The unaltered tuff is greenish in colour, and is speckled pink and white by reason of the larger sub-idiomorphic felspar crystals. On weathering it turns brown and becomes pitted with holes where the calcite has been removed. These holes often contain a little limonite, and they are most frequently casts of crinoid ossicles or small shells. The tuffs vary greatly in texture. Those of finer grainsize are more resistant to erosion, and their outcrops may be traced through the hills. One band of medium grain gives rise to low hills about a quarter of a mile north-west of Wittitrin post office. Westward from here wonderful exposures of the series may be seen along Dungay Creek into the Parish of Boonanghi. The creek valley widens out, and generally receives a tributary creek where it crosses the broader mudstone bands, whereas the banks are precipitous in the tuff and sandstone regions.

The following section was measured along the limb of an anticline as one went west from Wittitrin post office. All the beds dip west at angles averaging about 15°.

|   | Thickness<br>in feet. |
|---|-----------------------|
| Blue sandstones and mudstones .. ..   | 225                   |
| Crinoidal felspathic tuffs .. ..  | 110                   |
| Fine conglomerate with <i>Loronema</i> (?),<br><i>Rhipidomella</i> , etc. .. .. | 30                    |
| Blue sandstones .. ..   | 170                   |
| Crinoidal felspathic tuff .. ..   | 100                   |
| Blue sandstones .. ..   | 185                   |
| Felspathic tuffaceous grit .. ..  | 45                    |
| Greenish-grey slates with worm tracks .. ..                                     | 100                   |
| Blue sandstone .. ..  | 45                    |
| Grey sandstone .. ..  | 240                   |
| Crinoidal tuffaceous grits and sandstones .. ..                                 | 140                   |
| Mudstones and sandstones .. ..  | 155                   |
| Crinoidal felspathic grit .. ..   | 150                   |
|   | <hr/>                 |
|   | 1,695                 |

This section is typical of the series. The total thickness of strata was not ascertained, as the basal beds were not

observed. There must be at least 4,000 feet of sediments, and in all probability many more.

Away from Dungay Creek, in rough country thickly covered with vegetation, neither the structure nor the sequence could be followed. Pieces of crinoidal felspathic tuff found in this locality indicate that the Boonanghi Series outcrops over a large area of country west of that now being described. Mudstone has been revealed by a creek in portion 172, and dips in a north-easterly direction at 25°. This unit, which resembles the other Boonanghi mudstones, varies somewhat in its texture, and shows worm tracks and other markings, possibly rain prints and sun cracks. It is hardly laminated sufficiently to be termed a shale, but is banded, and breaks up into small flaggy blocks. The underlying beds are crinoidal tuffs, but the overlying rocks have been cut off by a fault and Kullatine strata take their place.

The fossil content of the Boonanghi Series indicates that its age is Lower Carboniferous, and that it may be correlated with the Burindi Series of the Hunter Valley.

There is sufficient doubt with regard to its exact limits to justify the adoption of the new name of Boonanghi, after the parish in which the maximum development takes place.

#### Middle to Upper Carboniferous: The Kullatine Series.

The lower beds of the Kullatine Series consist of sandstones, tuffs, sandy tuffs and breccias showing a great deal of variation in texture and composition, but possessing a general dark or light grey colour (DR 3125 and DR 3128). All are very hard and resistant to weathering, forming a conspicuous range of hills which, though dissected by streams, continues in a huge semi-circle towards Moparrabah. The steep slopes in this region and thick vegetation in the gorges make progress very slow or impossible, so that geological investigations are most difficult.

These tuffaceous rocks may be seen in Portions 189, 190 and 165 and in the Boonanghi State Forest. They must represent several thousands of feet of material, but no reliable estimate could be obtained. The tuffs pass upwards into thinly bedded cherts and mudstones containing well preserved *Aneimites*, *Rhacopteris* and tree trunks. These beds bring in a marked change in the physiography, as the tuff hills which form the divide



between Dungay and Commong Creeks fall rapidly towards the east and north-east.

The first discovery of *Aneimites in situ* in this district was made in the creek near a clearing close to the centre of Portion 190. A good collecting ground for the plants, doubtfully regarded as the same horizon as above, is on Portion 189 on a bluff close to Dungay Creek and in the gully to the west (DR 3096 to DR 3127). Fossil wood was found among grits, sandstones, cherts, etc., on Portion 177 at Dondingalong (DR 3090 to DR 3095).

Following the plant beds we have the glacial stage of the Kullatine Series, composed largely of dark grey tuffs interbedded with fluvio-glacial conglomerates and grey varve shales. Volcanic activity has continued throughout the glacial period (DR 3097 to DR 3104). The conglomerate bands contain water-worn pebbles, mostly well rounded, but intermixed with some very irregular ones. Some of the boulders are two feet in diameter, and erratics of pink granite somewhat larger than this were seen. These possessed most irregular boundaries, and fragments broken from them and just hanging or slightly separated left little doubt as to their origin. Some of the conglomerates are best described as being fluvio-glacial. Typical rocks included in them are pink and grey granites, white quartz, quartzite and many varieties of porphyries and sandstones.

The varve shales are neither as abundant nor as noticeable as in the Hunter River or Currabubula Districts, and are very different in appearance, being dark grey, cherty, and, though possessing some summer and winter layers, are more typically fine-grained rocks not markedly laminated. The continual deposition of volcanic ash into the lakes in which they were being laid down largely determined their characteristics.

Excellent exposures of the glacial beds are to be seen in Portions 190, 168 and 169. They form the foothills of the main range, and their junction with the overlying Macleay Series is marked by a definite break in slope. At Dondingalong these conglomerates and tuffs are responsible for Gowing's Mount, which attains a height of over 700 feet in Portions 176 and 183. They outcrop also in Portions 177, 200 and 163, just north of Dungay Creek, and are associated with the underlying plant beds. All continue southwards into the Parish of Wittittrin, where

they again form high hilly country and swing round to join up with the Yessabah formations south of the Caves.

On the eastern fall of Gowing's Mount a splendid outcrop of tillite occurs. It consists of numerous angular rock fragments of great variety, set in a bluish-grey ground mass, which weathers to a purplish colour. Because of this colouring it was first thought to belong to the Tait's Creek glacial horizon in the Macleay Series, but has now been included in the Kullatine division. As S. W. Carey (verbal communication) suggests, it is comparable with the tillite described by him from the top of the Kuttung Series in the Currabubula District (DR 3083 to DR 3091).

A correlation of the Kullatine Series with the Kuttung Series in the Paterson and Currabubula Districts is confidently made.

#### Permian: The Macleay Series.

The tillite at Dondingalong does not appear to extend very far, and the grey tuffs of the Kullatine Series at Yessabah are followed in places by the purple Tait's Creek glacial beds and elsewhere by fossiliferous sandstones and tuffs of the Macleay Series. The junction line is very difficult to pick up, more because of the very poor outcrops than because of any similarity in rock type.

Although the writer does not suggest that there is any unconformity between the Kullatine and Macleay Series, the removal of some of the topmost beds of the older series is indicated by the variation in the nature of the rock upon which the younger series rests. There must have been an important time break represented by this disconformity, and it involved a change over from terrestrial to marine conditions.

After its junction with the Wittitrin road, the Willi Willi road follows a belt of purple calcareous shales and tuffs containing scattered pebbles which are faceted and striated. Here the beds are at the base of the Macleay Series. They were first described by Dr. W. G. Woolnough<sup>(12)</sup> and called the Tait's Creek glacial beds, from their occurrence to the west; he correlated them with the Lochinvar glacial beds in the Hunter Valley. The rocks are generally purple or red in colour, but rarely grey, green and blue; as they are soft and subject to deep weathering, it is uncertain what is the colour of the fresh rock. The only exposures seen were where road cuttings had been made or where a creek had recently been eroding

its banks. Pebbles collected from the shales mainly off Portions 98 and 142 included the following:

Pink acid granite (coarse and fine types).

Purple rhyolite with pink orthoclase phenocrysts and chlorite amygdales.

Orthoclase porphyry with pink and white felspar phenocrysts up to 5 mms. in diameter set in a purple ground mass.

Quartz porphyry with rounded quartz phenocrysts.

Hornblende andesite.

Banded purple andesite.

Glassy andesite with tabular plagioclase phenocrysts.

Keratophyre; green dacite.

Dacite with quartz and plagioclase crystals set in a dark brown groundmass.

Grey sandstone, brown quartzite, green quartzite, etc.

Their sporadic distribution, striations, facets and angular shapes leave no doubt that the above pebbles had a glacial origin. Some water-worn pebbles were found, but these were subordinate in quantity to the others (see specimens DR 3020 to DR 3028).

A microscopic section of a typical piece of the containing rock showed it to be a tuff composed of angular quartz grains up to 0.1 mm. in diameter and fragments of volcanic material up to over 3 mms., all set in an opaque groundmass, deep brown by reflected light. The volcanic material is ragged in outline, and consists of chlorite with tabular, somewhat decomposed feldspars, and a little quartz. The groundmass is largely hæmatitic. The rock reacts violently with hydrochloric acid owing to the presence of calcite derived from the marine fossils which occur plentifully in it. Among the fossils found in this unit are crinoid stems, Fenestellidæ, *Spirifer* sp., *Martiniopsis subradiata*, and small lamellibranchs.

The following sequence was measured along a branch of Commong Creek in Portions 190 and 191:

|                                      | Thickness<br>in Feet. |
|--------------------------------------|-----------------------|
| Fine-grained grey tuff .. ..         | 130                   |
| Purple chert with sponge spicules .. | 15                    |
| Purple tuff with pebbles .. ..       | 10                    |
| Brown tuff .. ..                     | 20                    |
| Silicified limestone (Zone "D") ..   | 40                    |

|   |           |
|---|-----------|
| Crinoidal limestone (Zone "C") ..   | 240       |
| Fenestellidæ mudstone and pecten sandstones, etc. (Zone "A"), with possibly some purple glacial beds .. | 350       |
|   | <hr/> 805 |

(Australian Museum Collection, DR 3011 to DR 3028.)

The differences between the above sequence and that given below from Dondingalong, measured along creek at north end of Portion 158, will be readily appreciated.

|  | Thickness<br>in Feet. |
|--|-----------------------|
| Grey mudstone .. .. .                                    | ?                     |
| Sandstone with pectens (Zone "E") ..                     | 90                    |
| Silicified limestone (Zone "D") ..                       | 70                    |
| Crinoidal limestone (Zone "C") ..                        | 100                   |
| Fenestellidæ mudstone (Zone "B") ..                      | 20                    |
| Limestone .. .. .  | 10                    |
| Fenestellidæ mudstone (Zone "B") ..                      | 20                    |
| Sandstone with pectens, etc. (Zone "A2")                 | 40                    |
| Conglomerate with shell fragments<br>(Zone "A1") .. .. . | 15                    |
| Sandstone .. .. .  | 50                    |
| Conglomerate with shell fragments ..                     | 10                    |
| Sandstone and tuff (Zone "A") ..                         | 85                    |
|  | <hr/> 510             |

(Australian Museum Collection, DR 2985 to DR 3005.)

The occurrence of the glacial beds in these two localities is somewhat doubtful, but if present they are included in the basal sandstones and tuffs.

Overlying or replacing the glacial horizon is a variable thickness of sandstones and calcareous mudstones which are crowded with marine fossils. Between Portions 188 and 199, just east of the Wittittrin road, pectens are well preserved in mudstone, and are exceedingly numerous. *Ptychomphalina* is abundant wherever the pecten beds are found. The fossils contained in this bed are listed in the palæontology section of this paper as Zone "A". Good collecting grounds are at Dondingalong on the low ridges east and south-east of Gowing's Mount, and also at Yessabah in Portion 165 near the stock route. The

sandstones and mudstones thin out rapidly northwards, so that when the purple glacials become well represented in Portion 109, they are only a few feet thick, and the crinoidal limestone rests almost directly upon the glacial beds. The Fenestellidæ mudstone horizon which is between the limestone and the pecten beds at Dondingalong has almost disappeared. It is noteworthy that, south of Willi Willi, the sandstone, mudstone and tuff beds between the limestone and the glacial beds are at least 750 feet thick, being even better represented than in the parish of Kullatine (specimens DR 3042 to DR 3082). Here the sediments are more clearly divisible into separate beds. Conglomerate occurs, and some of the mudstones form definite Fenestellidæ horizons. Other beds are full of *Productus brachythærus* (?) (specimens DR 3042 to DR 3082).

Details of the sandstones and mudstones at Yessabah are difficult to obtain owing to the scarcity of outcrops, but at Dondingalong two thin bands of conglomerate were mapped among the more finely grained sediments. These conglomerates contain fragments of large shells, probably pectens, among rounded and sub-angular pebbles. *Spirifer vespertilio* has been identified also. At Dondingalong the topmost beds of this fossil zone are calcareous mudstones crammed with Fenestellidæ and productids. The forms collected from here include *Linoproductus springsurensis* and *Monilopora* cf. *nicholsoni* (see Zone "B" list). The bed is well exposed on Portions 173 and 183, where it outcrops in the form of large flaggy boulders. When fresh it is a grey colour, and contains fossils composed of crystalline calcite. These are best detected on the weathered surfaces.

The mudstone contains limestone bands and passes upwards into the main horizon of crinoidal limestone. This unit may be traced from south of the lime station near Kundabung north-westward to Dondingalong, and then, with breaks due to faulting, from Yessabah to the west and south-west of Willi Willi. Because of the proximity of the limestone to the purple glacial beds on the Willi Willi road, and the association of the limestone with the fossiliferous sandstones and mudstones at Yessabah and Dondingalong, the question arises whether the limestones are on the same horizon in each case. Although there is an impure limestone band fifty feet thick and about 500 feet above the main limestone horizon in the parish

of Warbro, no evidence was found to support the idea that there are two main limestone horizons in the sequence. The very fact that sections taken in various localities throughout the Macleay Series do not correspond in detail is evidence enough of the discontinuity of certain of the beds. The limestone, indeed, seems to be the only horizon upon which it is safe to rely.

The limestone band varies from 100 feet to 500 feet in thickness. It is crystalline, fairly even in texture throughout, and almost pure calcium carbonate in its composition. Its appearance is attractive and unique, the colour being usually pink, but also reddish-brown, purple, grey and white. It would make an excellent ornamental building stone, being obtainable in large blocks at numerous localities. The columns at the entrance to the Art Gallery in Sydney bear testimony to its appearance. Even better material could be obtained (specimens DR 2986 to DR 3004). On weathering, the surface of the limestone becomes grey. The effect of weathering is well seen in the fluted outcrops at the Caves Hill, Yessabah. Here, too, are a number of small caves with stalactites and shawl formations. Similar caves are found at Moparrabah and Willi Willi.

Fossils are best detected on the weathered surfaces of the limestone, which is largely made up of crinoid ossicles. Under the microscope many bryozoans were also seen (see fossil list for Zone "C"). *Eurydesma cordatum* has been found in abundance in the Willi Willi District in association with large pectens.

Though massive in places, the rock sometimes is seen lying in beds of variable thickness, between which there is a little sediment. Sometimes patches of pebbles are found in the limestone, and their presence suggests that they might have been dropped from icebergs still lingering after the passing of the main glacial epoch. That marine fossils form the limestone and that they actually occur in the purple glacial beds indicate that these forms of life were able to live under comparatively cold conditions.

Tuffaceous material is much in evidence, showing that volcanoes were still active. It would seem that much of the reddish colouring of the limestone is due to the addition of fine volcanic ash during its deposition. The crinoidal limestone is followed by silicified limestones, which vary greatly in their characteristics from bed to bed. They are well exposed by the creek running through Portion 158.

On weathering, the calcium carbonate is removed and spongy siliceous masses remain. As the silica has, for the most part, replaced the fossils, these are splendidly preserved. *Monilopora* cf. *nicholsoni* is most abundant in this zone, so that much of the resulting material resembles macaroni (see Zone "D" fossils). On top of the silicified limestone is a variable thickness of tuffaceous sandstone containing pectens. It is well exposed at Dondingalong, but generally forms poor outcrops.

The beds described above are the only ones traced with any degree of certainty in the parish of Kullatine. The mudstones, tuffs and sandstones overlying them give rise to few outcrops, and attempts to map them even broadly have met with little success. Whether the sediments pass upwards into the Kempsey Series, or whether they are separated therefrom by faulting, is not known. The mudstones are soft, crumbly, and black and are exposed in places by the creek in Portions 188 and 158.

#### Permian (?): The Kempsey Series.

This name has been given to the sandstones, slates, mudstones and tuffs which outcrop between Sherwood and Kempsey. There is little evidence to show what age the beds are, but as the writer has been unable to separate them from the Macleay Series, and as their outcrop corresponds with the general structure of the Parrabel Anticline, he has considered them to be Permian. The general criteria used for identifying the beds have been given previously.<sup>(8)</sup>

The rhythmically bedded sandstones and mudstones in the eastern portion of the parish of Kullatine are doubtfully referred to the Kempsey Series. They are revealed by the road cuttings between Sherwood School and a point about a mile west, where they are covered by gravel deposits, and here are about a mile east of the Macleay Series limestone, which is dipping eastward. It would appear that these sediments, at any rate, are Permian in age and overlie the Macleay Series, but whether the same could be said truthfully about the beds further to the east is problematical.

For rocks referred to the Kempsey Series, see Australian Museum Collection, DR 2908 to DR 2984.

#### Pleistocene.

Gravel deposits cap many of the hills in the parish of Kullatine, and, in fact, much of the country between

Sherwood and Kempsey. They are well seen in road cuttings between Sherwood and Yessabah, where they have been cemented into a conglomerate and unconformably overlie the Permian rocks. Here they contain rounded jasper, quartz, chert and quartzite pebbles up to six inches in diameter. The age of these gravels is probably Pleistocene, because they appear to have been laid down by the Macleay River or its tributaries on the floor of a valley which had been carved by the river out of the plateau formed by uplifts closing the Tertiary era.

### PALÆONTOLOGY.

#### Boonanghi Series.

The crinoidal felspathic tuffs contain *Loxonema* sp., *Rhipidomella*, *Fenestella* sp., small gasteropods and lamelli-branches and numerous crinoid stems. Fragments of plant stems are common. The above collection, though small, indicates that the beds are Lower Carboniferous, and can probably be correlated with the Burindi Series of the Hunter River District.

#### Kullatine Series.

Fossil plants collected were *Rhacopteris*, *Aneimites* (?), and probably *Dadoxylon*. These are typically Middle to Upper Carboniferous forms, and there can be no reasonable doubt that the Kullatine Series and the Kuttung Series were contemporaneous.

#### Macleay Series.

From various sources, including specimens found in the Mining Museum, Sydney, and collected by Mr. J. E. Carne, the following list of the fauna recorded from the Macleay Series has been compiled :

(Descending order.)

#### SANDSTONE (Zone "E").

*Pecten* sp.

#### SILICIFIED LIMESTONE HORIZON (Zone "D").

*Fenestella* cf. *fossula*.

*Fenestella* cf. *internata*.

*Protoretapora* cf. *ampla*.

*Zaphrentis* (two species).

*Trachypora wilkinsoni*.

*Monilopora* cf. *nicholsoni*.

*Stenopora* (small dendroid form).



*Tribrachiocrinus corrugatus*.  
 Crinoid stems and plates.  
*Chonetes* sp.  
*Dielasma* sp.  
*Productus* cf. *subquadratus*.  
*Productus* sp.  
*Strophalosia gerardi*.  
*Martiniopsis subradiata*.  
*Spirifer* (four species).  
*Aviculopecten mitchelli*.  
*Merismopteria macroptera*.

#### LIMESTONE HORIZON (ZONE "C").

Sponge spicules, possibly *Lasiocladia* and *Hyalostelia*.  
*Monilopora* cf. *nicholsoni*.  
*Trachypora wilkinsoni*.  
*Zaphrentis gregoriana* De Kon.  
*Zaphrentis* sp.  
*Fenestella internata* Lonsdale.  
*Fenestella fossula* Lonsdale.  
*Fenestella propinqua* McCoy?  
*Protoretepora ampla* De. Koninck.  
*Phyllopora* cf. *Retepora* (?) De Koninck.  
*Stenopora* sp.  
*Martiniopsis subradiata* G. Sby.  
*Martiniopsis oviformis* McCoy.  
*Spirifera tasmaniensis* G. Sby.  
*Spirifera vespertilio* G. Sby.  
*Spirifera* spp.  
*Productus semireticulatus* Martin (?).  
*Productus brachythærus* G. Sby.  
*Productus* cf. *undatus* DeFrance.  
*Strophalosia* sp.  
*Eurydesma cordata* Morris.  
*Dellopecten illawarrensis* Morris.  
*Aviculopecten squamuliferus* Morris.  
*Aviculopecten mitchelli*.

Crinoid stems make up the greater part of the limestone in which the above forms occur.

#### FENESTELLIDÆ MUDSTONE (ZONE "B").

This bed is made up of masses of Fenestellidæ, but as well as these the following were collected:

*Monilopora* cf. *nicholsoni*.  
*Zaphrentis* cf. *arundinaceus*.  
*Fenestella* sp.  
*Protoretepora* sp.  
 Crinoid stems.  
*Strophalosia* sp.  
*Strophalosia gerardi*.  
*Productus* sp.  
*Pustula*.  
*Linoproductus springsurensis*.  
*Syringothyris* sp.  
*Spirifer vespertilio*.

*Spirifer* sp.  
*Martiniopsis subradiata*.  
*Conularia*.

PECTEN SANDSTONE AND MUDSTONE (ZONE "A").  
 (INCLUDING A1 AND A2.)

*Fenestella* sp.  
 Crinoid stems.  
*Martiniopsis subradiata*.  
*Spirifer* mult. spp.  
*Syringothyris*.  
*Aviculopecten sprengeri*.  
*Aviculopecten tenuicollis*.  
*Aviculopecten mitchelli*.  
*Cardiomorpha* (?).  
*Astartila* sp.  
*Ptychomphalina*.  
*Platyschisma* sp.

From the Macleay District De Koninck<sup>(5)</sup> described certain fossils, which he identified as:

*Favosites polymorpha* Goldf.  
*Chonetes hardensis* Phillips.  
*Chonetes coronata* Conrad.  
*Atrypa reticularis*.  
*Aviculopecten etheridgei* De Koninck.  
*Aviculopecten mcLeayi* De Koninck.

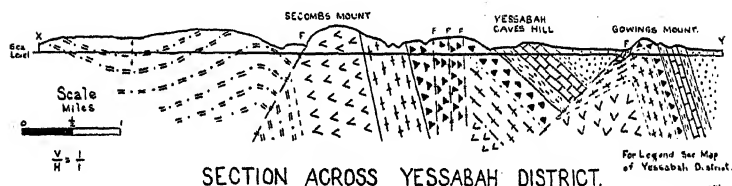
He had been led to believe that these were Devonian in age, but his description of the material in which they were preserved leaves little doubt as to the horizon. (Zone "A.")

From the above list of forms it seems that the Macleay Series may be correlated with the Lower Marine beds of the Kamilaroi Series in the Hunter Valley, and an attempt will be made later to show that the Drake Series of Boorook and Drake and the fault-block series of Silverwood, Queensland, also belong there. The writer prefers to call all these beds Permian owing to the lack of any convincing evidence to the contrary.

#### GEOLOGICAL STRUCTURES.

The strata in the parish of Kullatine form part of the eastern limb of the Parrabel Anticline or Anticlinorium, which pitches in a northerly direction.<sup>(8)</sup> Within the area described, complicated faulting has taken place. The conditions arising from this have brought about some interesting topographical results. Gowing's Mount, for instance, is an isolated hill which (obviously) has been more resistant to erosion than the surrounding rocks.

Actually it is a hard mass of Carboniferous conglomerates and tuffs brought by folding and faulting into the midst of the younger rocks. To the south-west of the Mount, patches of limestone occur under rather puzzling circumstances. They are sometimes in contact with carboniferous beds, and at other times with fragments of rocks associated with them elsewhere, but differently disposed. By tracing these blobs and other anomalies, one was led to a point south of Dungay Creek, where the Yessabah limestone turned to run east and west before being truncated by the Carboniferous conglomerates. It was then apparent that a fault (a) had moved the limestone about two miles to the north-east. The limestone masses which were so puzzling had been dragged along the fault-plane into these positions.



SECTION ACROSS YESSABAH DISTRICT.

Fig. 2.

Another large fault (b), resulting in an equivalent amount of movement, explains the break in continuity of the Yessabah limestone to the north. The paucity of outcrops makes the accurate location of this fault an impossibility, but its position as shown on the map has been inferred from the outcrops available. The strata around Gowing's Mount have been extensively folded and faulted, as shown by Map 2. The most conspicuous fault is that which runs near the north-western corner of Portion 137 and the north-eastern corner of Portion 200 (fault (c)). Movement along this has dragged the limestone westwards into a sharp fold, which can be seen to advantage in Portion 173.

Minor faults associated with the major ones have resulted in the twisting and movement of some beds into seemingly anomalous positions. The limestone of the Macleay Series is in contact with the Kullatine conglomerates in Portions 163 and 176, and explanations are very difficult. Strike faults in Portions 173 and 157 have further complicated the situation, and further north, in line with these, the

# GOWING'S MOUNT

## LEGEND

- RECENT. Alluvium
- PERMIAN
- MACLEAY SERIES
- Gray Mudstone.
  - Sandstone.
  - Siltified Limestone.
  - Crinoidal Limestone.
  - Fenestella Mudstone.
  - Conglomerate.
  - Sandstones and Mudstones.
- CARBONIFEROUS.
- KULLATINE SERIES.
- Glacial Beds.
  - Plant Beds.
- PROBABLE FAULTS.

SCALE

CHAINS

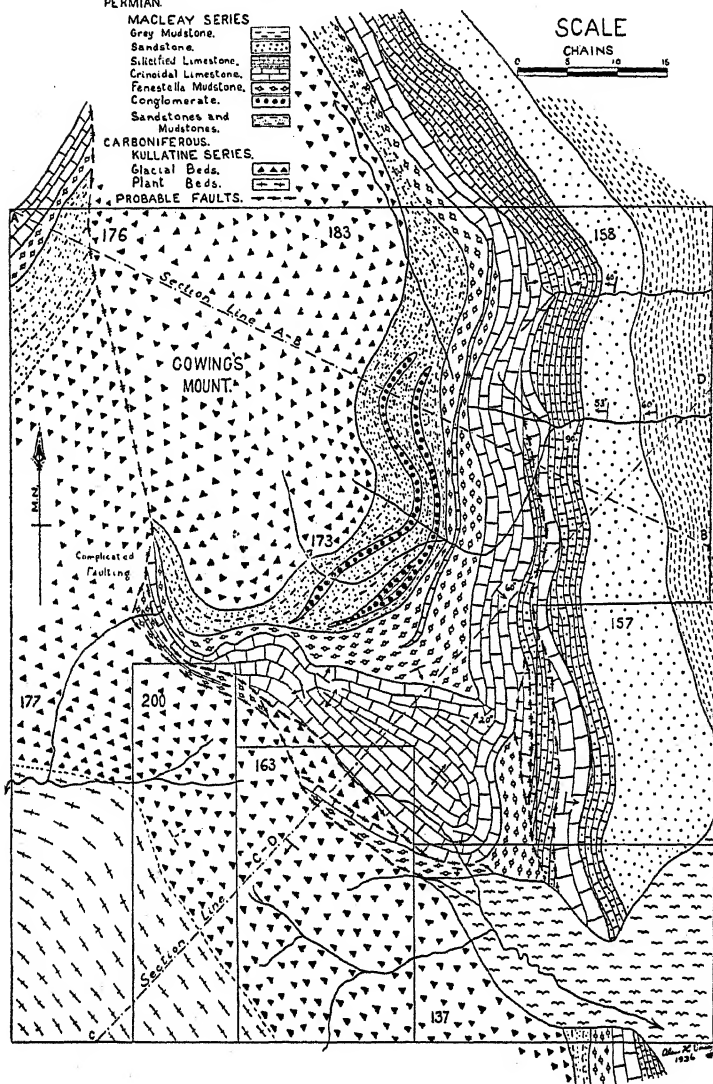


Fig. 3.

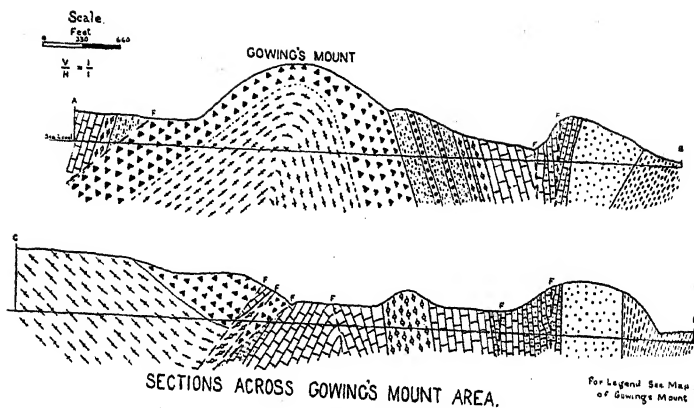


Fig. 4.

# SUGGESTED STAGES IN THE DEVELOPMENT OF THE YESSABAH FAULTS.

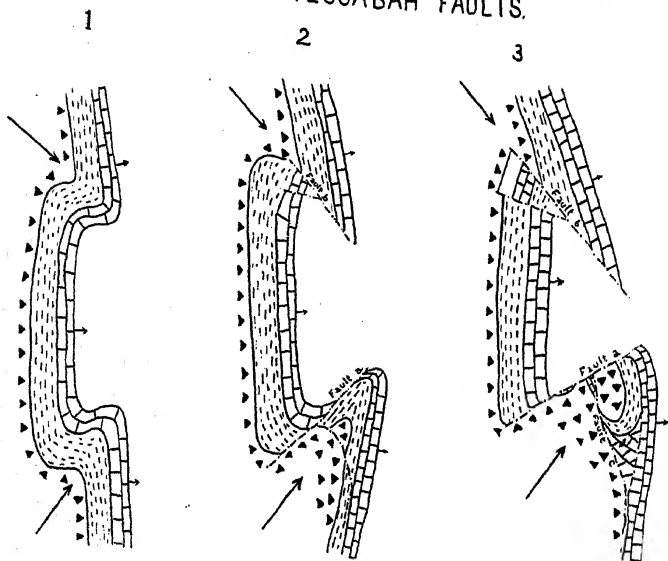


Fig. 5.

beds are overturned (Portion 158). Instead of dipping easterly as they do in the northern creek, those in the southern creek are dipping west or are vertical. Small folds and faults are apparent in many places, but it was impracticable to show them even on the large scale map. The area is recommended to anyone interested in structural geology, for there is still plenty of work to be done in it.

At Yessabah the limestone band dips easterly for the most part, but near the faulted area beside Dungay Creek it has been overturned and dips westerly. The dips range from  $40^{\circ}$  to  $90^{\circ}$  to the east or west along the extent of the outcrop. It seems that the Dondingalong beds on the south and the Willi Willi Road beds on the north were once continuous with the Yessabah beds, but, when fracturing took place, they were separated from each. The collapse of the eastern limb of the huge Parrabel Anticline is the probable explanation, and has been sufficient to cause the faulting and folding. A suggestion explaining the stages in the development of the structures is shown in the accompanying diagrams. The effects of this disturbance have extended into the beds of the Kullatine Series. These in some areas are vertical or possess reversed dips, although the strata generally dip east. Strike faulting is well developed.

The Boonanghi Series to the west has suffered little deformation. The beds have been folded on a north-south axis into gentle undulations which pitch north. Dips are generally from  $5^{\circ}$  to  $10^{\circ}$ , rarely reaching  $15^{\circ}$  or  $20^{\circ}$ . It is rather interesting to observe the large areas of older rocks so little disturbed, while the younger ones have been excessively faulted and folded only a mile or two away.

#### PHYSIOGRAPHY.

The physiography bears a most direct relationship to the nature of the rocks. It may be stated quite generally that the Kullatine rocks can be picked out immediately from the rocks of the Macleay Series because they occupy the points of greatest relief. The Caves Hill, composed of limestone, is the only prominent feature produced by other than Carboniferous rocks.

The main range of hills which can be seen by looking west from Kempsey to Sherwood consists of Kullatine strata. The highest points are composed of the lower tuffaceous beds, while the fluvio-glacial conglomerates form the foot-hills; Gowing's Mount, which is quite conspicuous by

reason of its grassy eastern slope, is mainly conglomerate. East of Gowing's Mount there are two ridges, the first of the pecten sandstone (Macleay Series) and the second of silicified limestone and the overlying sandstone. These two ridges are separated by limestone, which, as usual, occupies the gullies. The pecten sandstone swings west, while a flat between this and the Kullatine hills southward is carved out of limestone.

The Caves Hill owes its relief to the silicified limestone band, which forms a hard protective capping. The eastern dip of  $40^\circ$  is low enough to make this capping effective. Where the beds are vertical, or nearly so, the silicified limestone forms low ridges and the limestone hollows. Further to the north-west, where the dip becomes more gentle, there happens to have been less silicification, so the limestone does not give rise to high hills until Sebastopol is reached. Here the dip is north at about  $25^\circ$ , and the upper beds are silicified. A limestone range results.

West of the range of Kullatine rocks, which exceeds 1,300 feet in Secomb's Mount, there is rugged country, some of it composed of Boonanghi Series. Eastwards we find only grassy or wooded undulating hills. The soft beds overlying the Macleay Series occupy this region. Some of the hills are gravel-covered, but this is indicated usually only by the presence of rounded pebbles in the soil.

The physiographical history of a larger region including the parish of Kuttung has been described elsewhere.<sup>(9)</sup>

#### GEOLOGICAL HISTORY.

Probably simultaneously with the deposition of the Burindi beds elsewhere in New South Wales, the mudstones and tuffs of the Boonanghi Series were laid down during Lower Carboniferous times. Marine conditions prevailed to the accompaniment of explosive volcanic eruptions. During periods of inactivity greyish-green mudstones were deposited, while occasional floods washed in coarser material, giving rise to conglomerates and sandstones. While the volcanoes were active, the ash from them kept falling into the sea, covering the crinoids and other marine organisms. That most of the ash suffered little transportation is demonstrated by the fact that the feldspars in the tuff are sub-idiomorphic and undecomposed.

Uplift terminated the marine period, but volcanic activity continued throughout a time of fresh-water

conditions. Plants growing round the lake were washed into it and became buried in the finer muds. There followed a glacial epoch, icebergs floating on a sea fringed with active volcanoes. After an uplift and probably a period of erosion, there were subsidence and a marine transgression during Permian times. Crinoids, Bryozoa, corals and shell fish flourished under the closing stages of the glaciation. Though still active, the volcanoes no longer provided the bulk of the sedimentary material. It is likely that there was another change over to fresh-water conditions during the deposition of part at least of the Kempsey Series.

At the close of the Palæozoic era great folding movements took place, resulting in the development of the Parrabel Anticline. During the period of stress the eastern limb of the Anticline fractured, and adjustments by faulting gave rise to the complicated structures in the parish of Kullatine. Then came a long period of erosion and reduction of the land nearly to a peneplain, but leaving a comparatively low divide between the eastern and western rivers. The Kosciusko Uplift at the close of Tertiary times produced the highlands into which the Macleay cut its valley. Gravel deposits now found on the tops of low hills round Sherwood were laid down on an old valley floor which has since suffered dissection. The river and its tributaries are entrenched in this older valley.

#### CONCLUSION.

This paper is the first attempt to describe in detail the rocks outcropping in the Macleay District. It is far from complete, even for the small area discussed, because of the multitude of rock types and complex structures therein. Moreover, it has not been possible to have all the fossils identified. The question of correlation has been dismissed with a few words here, but will be discussed more fully in a subsequent publication.

#### ACKNOWLEDGMENTS.

I desire to thank Mr. L. L. Waterhouse for his assistance and advice in the compilation of this work, a great deal of which was done under his direction. My thanks are due also to Dr. Ida Brown and Messrs. H. O. Fletcher and F. Booker for the identification of fossils.

The collection of rocks and fossils is available for inspection at the Australian Museum, Sydney.



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## EXPLANATION OF PLATE VI.

Fig. 1.—View looking east from Gowing's Mount. (Kullatine Series, Glacial Stage.)

The first ridge is pecten sandstone; the white outcrops in the next valley are limestone; the second ridge, broken by creek, is silicified limestone. Poor outcrops in undulating country beyond.

Fig. 2.—Crescent Head.

Typical section of the Kempsey Series, showing rhythms in sediments and small fault.



Fig. 1.

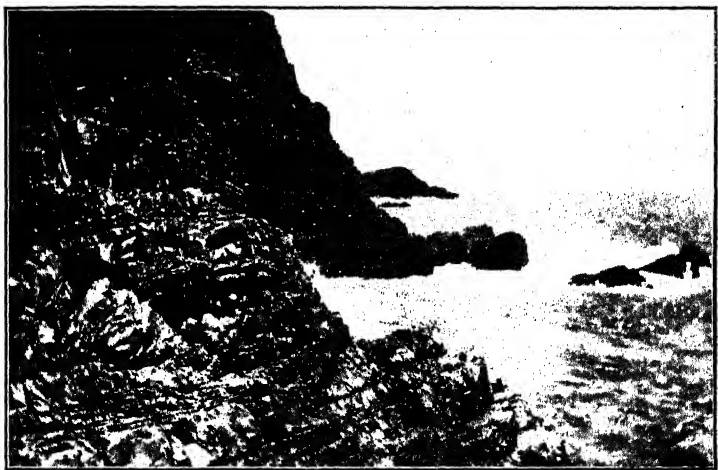


Fig. 2.



# THE OPTICAL PROPERTIES AND CRYSTAL STRUCTURE OF SOME COMPOUNDS OF THE TYPE $R_xMX_4$ .

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and F. M. QUODLING, B.Sc.

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In a previous communication (THIS JOURNAL, 1935, 69, 167) the optical properties of  $K_2[PdCl_4]$  and  $K_2[PtCl_4]$  were considered in relation to their crystal structure. The pronounced double refraction observed was attributed to the parallel, square co-ordinated  $[PtCl_4]^-$  and  $[PdCl_4]^-$  ions which occur in the structures of these crystals, since precisely the same considerations as were employed by Bragg (*Proc. Roy. Soc. Lond., A*, 1924, 105, 378) in accounting for the optical anisotropy of crystals containing  $NO_3^-$  and  $CO_3^{2-}$  ions may be used to explain the anisotropy of planar  $[MX_4]$  ions. Pauling (*Journ. Amer. Chem. Soc.*, 1931, 53, 1367) has shown from quantum mechanical considerations that square co-ordinated groups are to be expected also among four covalent cupric, auric and nickelous compounds. As yet the X-ray analysis of relatively few such compounds has been carried out, but where it has been achieved the crystal optics in general agree, qualitatively at least, with the structures proposed. For example in each of the structures  $K_2[PtCl_4]$ ,  $K_2[PdCl_4]$ ,  $[Pd(NH_3)_4]Cl_2 \cdot H_2O$ , and  $[Pt(NH_3)_4]Cl_2 \cdot H_2O$ , the refractive index is a maximum for any ray whose electric vector lies in the plane of the square co-ordinated ion. The very pronounced double refraction of several compounds of gold,  $(N(CH_3)_4)[AuCl_4]$ ,  $Na[AuCl_4] \cdot H_2O$  and also nickel ( $K_2[Ni(CN)_4] \cdot H_2O$ ), whose crystal structures have not yet been determined, is of interest. The strong double refraction cannot, however, be regarded as definite proof of the existence of square co-ordinated ions, since

other features\* of the structure may account for at least part of the double refraction. It does not seem likely, for example, that the whole of the double refraction of  $\text{LiK}[\text{Pt}(\text{CN})_4]3\text{H}_2\text{O}$ , 0.668 (see Winchell, "The Optic and Microscopic Characters of Artificial Minerals", p. 20) can be attributed to square  $[\text{Pt}(\text{CN})_4]^-$  ions. Nevertheless the double refraction in the case of the above compounds is so much more marked than that of any of the compounds of the type  $\text{R}_x\text{MX}_4$  (where  $\text{MX}_4$  is tetrahedral) that it is reasonable to consider it due, in large measure, to strongly anisotropic square co-ordinated ions.

Not only does the nature of the optical properties suggest these structural features, but furthermore it should serve as an additional and useful check on the orientation of planar groups as determined by X-ray structural analysis. Table I summarises the crystal optics of a number of substances of the type  $\text{R}_x\text{MX}_4$  where  $\text{M}=\text{Pt}$ ,  $\text{Pd}$ ,  $\text{Ni}$ ,  $\text{Cu}$ , or  $\text{Au}$ . Some of the constants have been taken from the literature, as indicated; otherwise the constants have been determined by the authors. Unless taken from sources where the accuracy was not stated, the refractive indices quoted are correct to  $\pm 0.002$ . They were measured by the immersion method with a sodium vapour lamp as a light source.

#### GOLD COMPOUNDS.

A preliminary announcement made in the present year (Huggins, *Journ. Chem. Educ.*, 1936, 13, 160) concerning the structure of tetragonal  $\text{N}(\text{CH}_3)_4[(\text{AuCl}_4)]$  states that  $[\text{AuCl}_4]$  groups are square co-ordinated, but nothing is said regarding their orientation. Since  $\text{N}(\text{CH}_3)_4[\text{AuCl}_4]$  is optically positive, a possible arrangement of the  $[\text{AuCl}_4]$  ions is for them to be parallel to "C" and so arranged along this axis to make  $90^\circ$  with each other. Attempts to measure  $\beta$  and  $\gamma$  for  $\text{K}[\text{AuBr}_4]$  were unsuccessful, because the immersion media used, methylene iodide solution of stannic iodide and phenyldiodo-arsine, rapidly

\* In the structure of  $\text{MgPt}(\text{CN})_4 \cdot 7\text{H}_2\text{O}$  alternate Mg and Pt atoms are arranged in rows parallel to the tetragonal axis [Bozorth and Haworth, *Phys. Rev.*, 29, 228 (1927)]. The distance between the atom centres in these rows is approximately 1.57A, while the shortest distance between the rows is 10.3A. This arrangement of the metal atoms would account for the strong positive double refraction. The orientation of  $[\text{Pt}(\text{CN})_4]^-$  groups previously suggested (THIS JOURNAL, 1935, 69, 167) is impossible if Mg and Pt atoms are arranged in the way deduced by Bozorth and Haworth.

TABLE I.

| Substance.                        | Symmetry.     | $\omega_D$<br>$\alpha_D$ | $\beta_D$         | $\epsilon_D$<br>$\gamma_D$ | Double<br>Refraction.         | Orienta-<br>tion of<br>Optic<br>Axial<br>Plane. | Optic Axial<br>Angle, etc.                       |
|-----------------------------------|---------------|--------------------------|-------------------|----------------------------|-------------------------------|---|--|
| $K_2[Ni(CN)_4] \cdot H_2O$        | Monoclinic.   | 1.440                    | 1.594             | 1.598                      | -0.158                        | 100   | $2V = 15^\circ 24'$<br>(calc.).                  |
| $N(CH_3)_4[AuCl_4]$ (1)           | Tetragonal.   | 1.616                    | —                 | 1.771                      | +0.155                        | —   | —  |
| $Na[AuCl_4] \cdot H_2O$ (2)       | Orthorhombic. | 1.545                    | ?                 | > 1.75                     | > +0.205                      | ?   | ?  |
| $K[AuBr_4]$ (3)                   | Monoclinic.   | < 1.74                   | > 1.74            | > 1.74                     | Medium to<br>strong negative. | 010   | $2V$ very small,<br>$CX = +13^\circ$ .           |
| $Os_2[CuCl_4] \cdot$ (4)          | Orthorhombic. | 1.625                    | 1.648             | 1.678                      | +0.053                        | 100   | $2V = 83^\circ 46'$<br>(calc.).                  |
| $[CuCl_2 \cdot 2H_2O]$ (5)        | Orthorhombic. | 1.66                     | 1.685             | 1.708                      | +0.06                         | 001   | $2V = 80^\circ 40'$<br>(calc.).                  |
| $[Pd(NH_3)_4]Cl_2 \cdot H_2O$ (6) | Tetragonal.   | 1.619                    | —                 | (calc.).                   | -0.060                        | —   | $\gamma = a$ .                                   |
| $K_2[PdCl_4]$ (7)                 | Tetragonal.   | 1.710                    | —                 | 1.559                      | -0.187                        | —   | —  |
| $[Pt(NH_3)_4]Cl_2 \cdot H_2O$ (8) | Tetragonal.   | 1.672                    | —                 | 1.523                      | -0.005                        | —   | —  |
| $K_2[PtCl_4] \cdot$ (9)           | Tetragonal.   | 1.683                    | —                 | 1.667                      | -0.130                        | —   | —  |
| $Ba_2[Pt(CN)_4] \cdot 4H_2O$ (10) | Monoclinic.   | 1.6706                   | 1.677<br>(calc.). | 1.553<br>1.8982            | +0.2276                       | 010   | $2V = 18^\circ$ ,<br>$\gamma C = -1^\circ 20'$ . |
| $Mg[Pt(CN)_4] \cdot 7H_2O$ (11)   | Tetragonal.   | 1.561                    | —                 | 1.910                      | +0.35                         | —   | —  |
| $LiK[Pt(CN)_4] \cdot 3H_2O$ (12)  | Orthorhombic. | 1.6237                   | 1.6278            | 2.2916                     | +0.6679                       | 100   | $2V = 19^\circ$ , $\gamma = C$ .                 |

(1) Bolland, *Sitz. Akad. Wiss. Wien*, 1910, 119, 275.(2) Bolland, *ibid. Groth. Chem. Krist.*, p. 238.(3) Mellor and Quodling, *This Journal*, 1935, 69, 167.(4) Kurnakow and Andrejewski, *Zeit. anorg. chem.*, 1930, 189, 137.(5) Winchell, "The Optic and Microscopic Characters of Artificial Minerals", No. 4, p. 15. *Univ. of Wisconsin Studies in Science*.(6) Gumbert, *Bull. Soc. Fr. Min.*, 1917, 40, 177.(7) Winchell, *ibid.*, p. 20. Some other hydrated platino-cyanides do not show very marked double refraction.

attacked the crystals. Since the crystals absorb light very strongly, no other attempts were made to determine the refractive indices.

#### PALLADIUM AND PLATINUM COMPOUNDS.

In a previous paper it was noted that the double refraction of  $K_2PdCl_4$  was greater than that of  $K_2PtCl_4$ . This is what one would anticipate from the fact that the interatomic distance Pd-Cl, 2.29 Å < Pt-Cl, 2.32 Å (Dickinson, *Journ. Am. Chem. Soc.*, 1922, 44, 2404).<sup>\*</sup> A similar effect can be seen with the isomorphous nitrates, carbonates and borates. The double refraction of  $KNO_3$  is greater than that of  $CaCO_3$  and that of  $CaCO_3$  is greater than that of  $ScBO_3$ . (N-O=1.36 Å, C-O=1.43 Å, B-O=1.55 Å.) (For the statement that the double refraction of  $ScBO_3$  is less than that of  $CaCO_3$ , see Goldschmidt and Hauptmann, *Nachr. Gesell. Wiss. Göttingen, Math.-Phys. Kl.*, 1932, 1, 59.)

A recent structural analysis of  $[Pd(NH_3)_4]Cl_2 \cdot H_2O$  (Dickinson, *Zeit. für Krist.*, 1934, 88, 281) places square co-ordinated groups parallel to 001. The crystal optics are in agreement with this orientation. The double refraction of  $[Pd(NH_3)_4]Cl_2 \cdot H_2O$  is not so great as that of  $K_2[PdCl_4]$ , a circumstance which is probably due in some measure to a smaller polarisability of co-ordinated  $NH_3$  groups as compared with that of the co-ordinated chlorine atoms. Since Pd-Cl, 2.29 Å > Pd-N, 2.20 Å, a slightly larger double refraction for  $[Pd(NH_3)_4]Cl_2 \cdot H_2O$  would have been expected, but the effect of different interatomic distances on the mutual interaction of the dipoles is outweighed by the difference in the polarisability of Cl- and  $NH_3$ . By using values for ionic refraction of Cl- and the molecular refraction of water stated in Wasastjerna's paper (*Soc. Sci. Fennica, Comm. Phys. Math.*, 1922-1923, 1, 5)  $R[Pd(NH_3)_4]^{++}$  is calculated to be 29.9. The very low double refraction of  $[Pt(NH_3)_4]Cl_2 \cdot H_2O$ , 0.005 (Kurnakow and Andrejewski, *Zeit. für anorg. Chem.*, 1930, 189, 137) is rather surprising in view of the fact that it has been suggested that this substance is probably isomorphous with  $[Pd(NH_3)_4]Cl_2 \cdot H_2O$ .

<sup>\*</sup>It should be pointed out that Pauling and Huggins (*Zeit. Krist.*, 1934, 87, 225) list the inter-atomic distances Pt-Cl and Pd-Cl as identical (2.31 Å). If this is so another explanation for the difference in double refraction of  $K_2PtCl_4$  and  $K_2PdCl_4$  must be sought—possibly in terms of the different refractivities of Pt and Pd.

(Dickinson, *loc. cit.*), a substance with strong double refraction. A small amount of  $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2\cdot\text{H}_2\text{O}$  was made by dissolving the green salt of Magnus ( $[\text{Pt}(\text{NH}_3)_4]\text{PtCl}_4$ ) in ammonia solution. The colourless crystals deposited from the solution showed extremely low double refraction and were optically negative, thus confirming qualitatively the observations of Kurnakow and Andrejewski. (See also Groth, *Chem. Krist.*, 258.) Further investigation of this substance is necessary. A partial analysis only of  $\text{Ba}[\text{Pt}(\text{CN})_4]\cdot 4\text{H}_2\text{O}$  and the isomorphous nickel and palladium compounds (Brasseur and Rassenfosse, *Zeit. für Krist.*, 1934, 88, 210; Piérard and Rassenfosse, *ibid.*, 1935, 99, 470) has been worked out. The high double refraction of  $\text{Ba}[\text{Pt}(\text{CN})_4]\cdot 4\text{H}_2\text{O}$  seems to indicate the presence of square co-ordinated  $[\text{Pt}(\text{CN})_4]^-$  ions rather than, for example, octahedral groups with two additional water molecules. The position of  $\alpha$  and  $\gamma$  should help in fixing the orientation of  $[\text{Pt}(\text{CN})_4]^-$  ions.

#### NICKEL COMPOUNDS.

No X-ray analysis has yet been made of the structure of  $\text{K}_2[\text{Ni}(\text{CN})_4]\cdot\text{H}_2\text{O}$ . However, the published structure of  $\text{K}_2[\text{Ni}(\text{C}_2\text{O}_4\text{S}_2)_2]$  is as the authors state (Cox, Wardlaw and Webster, *Journ. Chem. Soc.*, 1935, 1476) in agreement with the crystal optics. When the electric vector lies in the plane of the parallel planar chelated groups the refractive index is a maximum.

#### COPPER COMPOUNDS.

The structure proposed for  $[\text{CuCl}_2\cdot 2\text{H}_2\text{O}]$  (Harker, *Zeit. für Krist.*, 1936, 93, 136) places two water molecules and two chlorine atoms about copper in the form of a square co-ordinated group. This structure differs in two important respects from that of  $\text{K}_2\text{PdCl}_4$ . Instead of a square co-ordinated group of the type  $[\text{MX}_4]$ , we have one of the type  $[\text{MA}_2\text{X}_2]$  where A and X have very different polarisabilities. Furthermore the square co-ordinated groups are not parallel to one another. Hence the double refraction is not so great as for structures containing parallel planar groups. The polarisability of the  $[\text{CuCl}_2\cdot 2\text{H}_2\text{O}]$  molecule is a maximum along a line parallel to that joining the centre of the two chlorine atoms, a minimum along the normal to the plane of the molecule, and has an intermediate value along the line joining the



two water molecules. Even though the relative orientation of the molecules is known, it is not possible to predict the relative values of  $\alpha$ ,  $\beta$  and  $\gamma$  without a knowledge of the actual values of the principal optical polarisabilities of the molecules. Even then the mutual influence between the optical dipole moments of neighbouring molecules may be quite large. The medium to strong double refraction of such compounds as  $\text{Cs}_2[\text{CuCl}_4]$  and  $\text{K}[\text{AuBr}_4]$  cannot necessarily be regarded as indicating the existence of square co-ordinated groups in these crystals. Since, however, the groups, if square, are of the type  $\text{MX}_4$ , the correlation of crystal optics with structure will be simpler than for  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ .

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## THE REACTION OF CREATININE WITH 1, 3, 5-TRINITROBENZOL, 2, 4, 6-TRINITROTOLUOL, AND 2, 4, 6-TRINITROBENZOIC ACID.

By ADOLPH BOLLIGER, Ph.D.

(With one text-figure.)

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Up till 1936 trinitrophenol (picric acid) was the only colour reagent applied to the detection and determination of creatinine. Recently, however, it has been reported that 3, 5-dinitrobenzoic acid also gives a colour reaction with creatinine which is suitable for its colorimetric determination (Bolliger, A., *THIS JOURNAL*, 1936, 69, 224). This observation has already been confirmed by Benedict and Behre (*J. Biol. Chem.*, 1936, 114, 515). In the present communication the behaviour of other aromatic nitro compounds towards creatinine is described.

## TRINITROBENZOL.

1, 3, 5-trinitrobenzol (melting point  $63^{\circ}$ ) in water containing sufficient alcohol to keep it in solution, gives with alkali an orange-red colour which to some extent depends on the strength of the alkali added. Very dilute alkali produces no colour. A concentration of about 0.001N only produces a faint pink which fades again in about 5 to 10 minutes. Then up to a certain point the colour and its permanency increases with increasing concentration of alkali. The colour produced by the addition of alkali becomes much stronger if more alcohol is present. Consequently the reaction of creatinine with trinitrobenzol can best be observed in the presence of small amounts of alkali in a solution containing just sufficient alcohol to keep the trinitrobenzol in solution. Under these conditions a deep rust-red colour is produced by creatinine, which varies in intensity according to the amount of creatinine present and which is not seriously influenced by the reaction between trinitrobenzol and alkali.

*The Detection of Creatinine with Trinitrobenzol.*

The fluid to be examined should be colourless and of neutral reaction. Two millilitres of it are transferred to a test tube and 0.6 ml. of an 0.4% alcoholic solution of trinitrobenzol (melting point 63°) and 0.4 ml. of an 0.01N sodium hydroxide solution are added. The mixture is then allowed to stand at room temperature for about one hour. If approximately 1 mgm. per cent. of creatinine is present a pink colour is produced. Higher creatinine concentrations furnish a rusty red. Concentrations below 1 mgm. are of a faint watermelon-pink colour. Amounts as low as 0.1 mgm. of creatinine can still be detected with this reaction if the sample is compared with a blank. But only when from 1 mgm. up to 8 mgm. per cent. of creatinine are present is there an approximate quantitative relationship between colour and creatinine concentration; more than 8 mgm. require more of the reagent. The blank treated in the same way as the solutions containing creatinine exhibits an orange colour immediately after adding the reagent. The creatinine solutions at first also show a similar colour. This colouration, however, which is due to the reaction between trinitrobenzol and the sodium hydroxide, fades in the blank and becomes practically colourless within an hour, while the colour due to the creatinine present develops during this interval.

The modification of trinitrobenzol which melts at 122° C. behaves towards creatinine in an essentially similar way to the compound which melts at 63° C. The colour produced by the 122° modification, however, is slightly more intense. The same also applies to the blank, and the colour obtained with the 122° modification does not fade for several hours, as compared with the 63°, which fades within an hour. Probably for this reason the higher melting substance also shows greater sensitivity. Furthermore, the compound with the higher melting point is less soluble. Under the experimental conditions as described, some of the 122° modification always crystallises out during standing, while the 63° modification remains in solution.

**TRINITROTOLUOL.**

Trinitrotoluol is less soluble than trinitrobenzol and considerable amounts of alcohol are required to keep this compound in solution. On the addition of alkali an alcoholate of deep purple colour is formed. This makes

the observation of its influence on creatinine somewhat difficult. No marked colour reaction between creatinine and trinitrotoluol can be observed at room temperature, but on short heating in the presence of sodium bicarbonate a colour is produced in the presence of creatinine, while the blank remains almost colourless.

*The Detection of Creatinine with Trinitrotoluol.*

If one adds to 2 ml. of a fairly cold saturated creatinine solution 0.2 ml. of a 1% solution of trinitrotoluol and 0.2 ml. of a 4% solution of sodium bicarbonate and heats in a boiling water bath for a few seconds, then the creatinine solution takes on a brown-red colour, while the control takes on a faint purple colour. At this stage one removes the tubes from the water bath and cools. The brown-red colour of the creatinine solution remains permanent for several hours. The control fades and remains colourless. If one heats the solutions in the water bath too long, i.e., ten minutes or more, a secondary reaction takes place. The blank and the creatinine solution take on a deep brown colour.

TRINITROBENZOIC ACID.

Trinitrobenzoic acid has the properties of an alkalimetric indicator. A very small excess of alkali changes the colourless neutral solution of its alkali salt towards orange. On the addition of more alkali a red colour is obtained. These solutions, on standing, change towards yellow.

If trinitrobenzoic acid is added to an alkaline solution of creatinine containing about 5 mgm. per cent. or more, a deep red colour is produced which remains permanent for days. Therefore, in order to avoid as much as possible the interfering colour which results from the reaction of trinitrobenzoic acid and alkali *per se*, it is advisable to take as little as possible of the alkali, if one aims at the detection of creatinine. On the other hand, experience has shown that it is preferable to use a large excess of trinitrobenzoic acid.

*The Detection of Creatinine with Trinitrobenzoic Acid.*

The fluid to be examined should be colourless and of neutral reaction. Two ml. of it are transferred to a test tube. Into another test tube which serves as a blank, 2 ml.

of water are placed. To both test tubes are now added 0.2 cc. of a 10% solution of sodium trinitrobenzoate. This is prepared by adding carefully, in small portions, 9.5 ml. of 0.4N sodium hydroxide to one gram of trinitrobenzoic acid. Immediately after the addition of a fraction of the sodium hydroxide, the mixture has to be shaken vigorously till the red colour disappears. Then carefully drop by drop 0.3 ml. 0.01N sodium hydroxide are added to the specimen as well as to the blank. Both blank and specimen now take on an orange tinge, which in the presence of about 1 mgm. of creatinine is distinctly deeper in the specimen than in the blank. Then both tubes are warmed over a flame till they just begin to boil; after this they are allowed to cool and the blank and specimen are compared in about half an hour after the heating. A red colour is obtained if 1 mgm. of creatinine or more is present in the specimen. This colour remains for several hours. Creatinine values of more than 5 mgm. per cent. furnish deep red shades which are permanent for more than a day. Values below 1 mgm. range from orange to yellow. On heating, the blank also takes on an orange-red colour, which, however, fades towards yellow on standing. Comparing blank and specimen, after standing for an hour, it is possible to detect with certainty concentrations of creatinine as low as 0.1 mgm. per cent. These small concentrations distinguish themselves from the blank by a deeper shade of yellow.

#### ON THE CHEMICAL NATURE OF THE COLOUR REACTIONS OF CREATININE WITH AROMATIC NITRO COMPOUNDS.

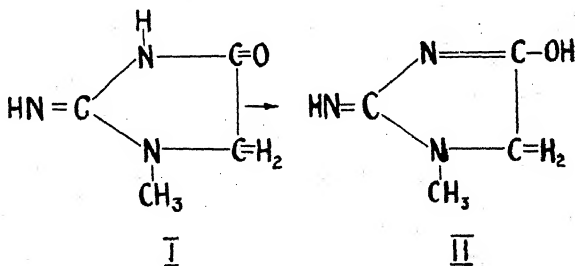
The colour reactions of creatinine with picric acid, 3, 5-dinitrobenzoic acid, 2, 4, 6-trinitrobenzoic acid, 1, 3, 5-dinitrobenzol, and 2, 4, 6-trinitrotoluol can probably be best explained as the formation of molecular compounds. Pfeiffer (*Z. Inorg. Chem.*, 1924, 137, 275; *Chem. Zeit.*, 1935, 59, 205), particularly, called attention to the fact that organic molecules like inorganic molecules frequently combine to molecular complexes. Furthermore, this author showed that the residual affinities which are responsible for the formation of these molecular compounds are localized in definite atoms or groups of atoms and are of a specific nature.

For example, it is well known that deeply coloured addition compounds are formed between nitrophenols

and aromatic hydrocarbons, such as the compound formed between picric acid and naphthaline. But not only trinitrophenol but also trinitrobenzol form similar molecular addition products which are also of the same colour. For instance, the organic complexes formed by trinitrobenzol and picric acid with anthracene are both deep red in colour. Such experiments are going to prove that not the hydroxol group is responsible for these reactions with aromatic hydrocarbons, but the nitro groups which are common to both types of compounds.

Creatinine may be considered as a hydrogenated imidazol, *i.e.*, 2-imido-3-methyl-3, 4-dihydro-5-ketoimidazol (formula I). Due to its basic properties it forms a well defined picrate of light yellow colour. On account of its non-aromatic character creatinine does not react with trinitrobenzol in neutral solution. However, as soon as a small amount of alkali is added, a deep red colour appears, which is due to the formation of an addition compound between the two molecules. With creatinine in the presence of alkali, similar deep colours are also produced by picric acid and trinitrobenzoic acid, while the compound formed with dinitrobenzoic acid is deep purple. On acidification these deep colours disappear and the components of the reaction can be recovered unchanged.

This reaction is in all probability due to keto-enolic change in the creatinine molecule (formulæ I and II) as brought on by the addition of alkali.



Creatinine, as represented by formula II, has now obtained aromatic properties and reacts like aromatic hydrocarbons or aromatic amines. The assumption of such a keto-enolic change is justified because Greenwald (*Am. Chem. Soc.*, 1935, 47, 1443) has shown that creatinine

derivatives with a substituted keto group such as the oxime are no further able to give a colour reaction with picric acid. Very recently this finding has also been confirmed with regard to dinitrobenzoic acid by Benedict and Behre (*J. Biol. Chem.*, 1936, 114, 515). The simultaneous existence in solution of two possible tautomers in the reaction of picric acid, dinitrobenzoic acid, etc., with aromatic amines has been demonstrated with optical methods by Ley and Grau (*Z. phys. Chem.*, 1922, 100, 271). In the case of creatinine similar conditions must be expected. Examination with the naked eye already confirms this. High concentrations of creatinine, however, give fairly uniform deep colours with the trinitro compounds tested, but with increasing dilution the colour changes towards yellow. The nitrophenolate or nitrobenzoate of creatinine are formed besides the molecular compound due to the residual valencies of the nitro groups. Such a colour change, of course, interferes with the colorimetric estimations of small concentrations of creatinine. Standard and unknown should be approximately of the same strength in order to obtain reliable results.

Among the substances mentioned, probably the best conditions with regard to the colorimetric estimation of creatinine are found in 3, 5-dinitrobenzoic acid. It is a practically colourless substance, in contrast to the strongly coloured picric acid. Even with the addition of a small excess of alkali as required by the colorimetric test the solution remains colourless in contrast to trinitrosodium benzoate, which, under similar conditions, turns red. In the case of 1, 3, 5-trinitrobenzol, similar conditions prevail as in the case of trinitrobenzoic acid, and the necessary presence of alcohol complicates the reaction still further. The reactivity of 2, 4, 6-trinitrotoluol is so small that this substance can not be considered of any use for the detection of creatinine.

#### SUMMARY.

New colour reactions of creatinine with 1, 3, 5-trinitrobenzol, 2, 4, 6-trinitrotoluol, and 2, 4, 6-trinitrobenzoic acid are described. These and similar reactions with picric acid and 3, 5-dinitrobenzoic acid have been explained as the formation of organic molecular compounds.

## ACKNOWLEDGMENT.

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COORDINATION COMPOUNDS OF CADMIUM WITH  
TERTIARY ARSINES.

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In a previous communication Anderson and Burrows (PROC. ROY. SOC. N.S.W., 1936, 70, 63-68) described compounds obtained from mercury salts and tertiary arsines. It was shown that two types of compound could be obtained,  $\text{HgX}_2 \cdot \text{R}$  and  $\text{HgX}_2 \cdot \text{R}_2$ , where R represents a molecule of tertiary arsine. It was found impossible to isolate a compound containing more than two molecules of arsine combined with one of a mercuric salt. Zinc and cadmium halides resemble those of mercury as regards their solubilities in organic liquids; the elements also have low atomic volumes. It was therefore decided to examine the compounds that could be obtained from cadmium and zinc salts with phenyl dimethyl arsine, diphenyl methyl arsine, and *o*- and *p*-tolyl dimethyl arsines. The cadmium derivatives are described in the present communication.

Compounds of cadmium halides with ammonia have been described containing one, two, three, four or six molecules of ammonia. These have generally been obtained in the dry way from the solid halide and ammonia. The most staple of these is of the type  $[\text{Cd}(\text{NH}_3)_4]\text{X}_2$ , which can be prepared in solution. In view of the stability of the 4-covalent complex cadmium ion it was thought that similar compounds containing one molecule of a cadmium halide coordinated with four molecules of a tertiary arsine might be obtained. Such, however, was not the case. Varying quantities of arsine were taken up to six molecules of arsine to one of cadmium halide. With the exception of bis-diphenyl methyl arsine cadmium iodide  $\text{Cd}(\text{Ph}_2\text{MeAs})_2\text{I}_2$ , in which two molecules of arsine are coordinated with one of cadmium, all of the compounds isolated contain one molecule of arsine to one of cadmium halide.

The arsine derivatives of cadmium halides are stable, colourless, crystalline compounds. The following table contains a list of the compounds isolated, together with their melting points :

|  | M.Pt.   |
|--|---------|
| Phenyl dimethyl arsine cadmium chloride .. ..                  | 220° C. |
| "          "          "          bromide .. ..                 | 186° C. |
| "          "          "          iodide .. ..                  | 108° C. |
| Diphenyl methyl arsine cadmium chloride .. ..                  | 292° C. |
| "          "          "          bromide .. ..                 | 257° C. |
| Bis-diphenyl "          "          iodide .. ..                | 100° C. |
| <i>o</i> -tolyl dimethyl arsine cadmium iodide .. ..           | 187° C. |
| <i>p</i> - "          "          "          "          " .. .. | 126° C. |

In the phenyl dimethyl arsine compounds it will be noticed that the melting point rises from iodide to chloride, corresponding to the variation in melting point of the cadmium halides themselves.

The compounds are all soluble in methyl and ethyl alcohols and in acetone, the iodide being the most soluble, particularly in acetone. Furthermore, with the exception of the iodides, solution is accompanied by decomposition, the arsine being apparently removed. The compounds could not be recrystallised. In order to recover the compound it is necessary to add excess of the arsine. Stability towards ether and benzene is in the same direction, but towards water or nitric acid the chloride is the most stable and the iodide the least, the latter decomposing in the cold, the former only on warming.

#### EXPERIMENTAL.

*Phenyl dimethyl arsine cadmium chloride*,  $\text{Cd}(\text{PhMe}_2\text{As})\text{Cl}_2$ , was prepared by adding a hot alcoholic solution of the arsine to cadmium chloride dissolved in a large volume of hot alcohol. On cooling the compound slowly separated in fine colourless needles melting at 220° C.

Found :  $\text{Cd}=31.3$ ,  $\text{Cl}=19.5$  per cent.

$\text{C}_8\text{H}_{11}\text{AsCl}_2\text{Cd}$  requires  $\text{Cd}=30.9$ ,  $\text{Cl}=19.5$  per cent.

*Phenyl dimethyl arsine cadmium bromide*,  $\text{Cd}(\text{PhMe}_2\text{As})\text{Br}_2$ , was prepared by mixing hot alcoholic solutions of the arsine and cadmium bromide and allowing to cool. After several hours a crystalline precipitate of cadmium bromide was removed, and the filtrate allowed to stand. A further precipitate of cadmium bromide was removed after twenty-four hours, and the solution allowed to stand for several weeks. Crystals gradually appeared, sometimes in the

form of large prisms and sometimes as fine feathery needles. The crystals melted at  $186^{\circ}\text{C}$ .

Found :  $\text{Cd}=25.4$ ,  $\text{Br}=35.4$  per cent.

$\text{C}_8\text{H}_{11}\text{AsBr}_2\text{Cd}$  requires  $\text{Cd}=24.8$ ,  $\text{Br}=35.2$  per cent.

*Phenyl dimethyl arsine cadmium iodide*,  $\text{Cd}(\text{PhMe}_2\text{As})\text{I}_2$ , was prepared by mixing alcoholic solutions of the arsine and cadmium iodide, concentrating on a water bath, and allowing to stand. After several hours colourless long prismatic crystals separated. These were filtered, washed with ether and recrystallised from alcohol and the product was found to melt at  $108^{\circ}\text{C}$ .

Found :  $\text{Cd}=20.2$ ,  $\text{I}=46.3$  per cent.

$\text{C}_8\text{H}_{11}\text{AsI}_2\text{Cd}$  requires  $\text{Cd}=20.5$ ,  $\text{I}=46.4$  per cent.

*Diphenyl methyl arsine cadmium chloride*,  $\text{Cd}(\text{Ph}_2\text{MeAs})\text{Cl}_2$ . An alcoholic solution of cadmium chloride was mixed with one of diphenyl methyl arsine and the mixture concentrated on the water bath and allowed to cool. After several hours colourless needles separated. They were removed by filtration, washed with alcohol and air dried. The compound melted at  $292^{\circ}\text{C}$ .

Found :  $\text{Cl}=16.8$  per cent.

$\text{C}_{13}\text{H}_{13}\text{AsCl}_2\text{Cd}$  requires  $\text{Cl}=16.6$  per cent.

*Diphenyl methyl arsine cadmium bromide*,  $\text{Cd}(\text{Ph}_2\text{MeAs})\text{Br}_2$ , was exceedingly difficult to prepare and was obtained only in small quantity. Cadmium bromide and the arsine (50% excess) were dissolved on the water bath in a large volume of alcohol, and then allowed to stand for several hours at room temperature. Cadmium bromide separated out and was removed by filtration. After several days fine prisms separated from the filtrate in small quantity. After careful washing with alcohol and drying at room temperature these were found to melt at  $257^{\circ}\text{C}$ .

Found :  $\text{Br}=31.1$  per cent.

$\text{C}_{13}\text{H}_{13}\text{AsBr}_2\text{Cd}$  requires  $\text{Br}=31.0$  per cent.

*Bis-diphenylmethylarsine cadmium iodide*,  $\text{Cd}(\text{Ph}_2\text{MeAs})_2\text{I}_2$ . This was the only compound that could be obtained when cadmium iodide was treated with the arsine, although the relative molecular proportions were varied over a wide range. To obtain the pure compound, equimolecular proportions of the constituents were dissolved in hot alcohol and the solutions mixed. On cooling, glistening long prisms separated in a few hours. These were removed

by filtration, washed with alcohol and dried at room temperature. The melting point was  $100^{\circ}\text{C}$ .

Found: I=29.5 per cent.

$\text{C}_{26}\text{H}_{26}\text{As}_2\text{I}_2\text{Cd}$  requires I=29.8 per cent.

*o*-tolyl dimethyl arsine cadmium iodide,  $\text{o-C}_7\text{H}_7\text{Me}_2\text{AsCdI}_2$ , was obtained by mixing hot concentrated alcoholic solutions of the arsine and cadmium iodide and allowing to stand. The compound separated in needles which were washed with alcohol, and on drying melted at  $187^{\circ}\text{C}$ .

Found: I=45.3 per cent.

$\text{C}_9\text{H}_{13}\text{AsI}_2\text{Cd}$  requires I=45.6 per cent.

*p*-tolyl dimethyl arsine cadmium iodide,  $\text{p-C}_7\text{H}_7\text{Me}_2\text{AsCdI}_2$ , prepared in a manner similar to the last compound, crystallised in thick prisms melting at  $126^{\circ}\text{C}$ .

Found: I=45.4 per cent.

$\text{C}_9\text{H}_{13}\text{AsI}_2\text{Cd}$  requires I=45.6 per cent.

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## DERIVATIVES OF ZINC HALIDES WITH TERTIARY ARSINES.

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In a previous communication (PROC. ROY. SOC. N.S.W., 1936, 70, 196-199) it was recorded that cadmium halides generally coordinate with tertiary arsines in the ratio of one molecule of arsine to one of cadmium salt. In the case of diphenyl methyl arsine and cadmium iodide, however, the ratio was found to be two of arsine to one of salt. No higher ratio could be obtained. This investigation was extended to the compounds formed with zinc salts, and it has been found that although the general tendency of zinc halides is to coordinate with two molecules of tertiary arsine, there is no evidence of zinc exerting a higher coordination valency towards these arsines.

While the compounds of zinc halides with these tertiary arsines, phenyl dimethyl arsine, diphenyl methyl arsine, *o*-tolyl dimethyl arsine, and *p*-tolyl dimethyl arsine are more easily formed than in the case of cadmium halides, the compounds themselves are less stable. They are all colourless crystalline compounds, and are deliquescent like the zinc halides themselves. This, together with the relative instability of the compounds in general, probably accounts for the fact that it was found impossible to isolate a derivative of zinc chloride and diphenyl methyl arsine, while the corresponding compound with phenyl dimethyl arsine had an indefinite melting point. Unlike the cadmium salts, the zinc compounds, with the exception of the iodides, always smell of the arsine, even after washing with ether or benzene. The iodides are comparatively stable, not deliquescent in moist air. The compounds are all soluble in alcohol and acetone; they also dissolve readily in ether, but the solutions quickly become cloudy, owing to the separation of zinc halides. Water immediately decomposes all of the compounds with the separation of

the arsine. As was found to be the case with the cadmium compounds the iodides are the least stable towards concentrated nitric acid, whilst the chlorides are the most stable.

#### EXPERIMENTAL.

*Phenyl dimethyl arsine zinc chloride*,  $\text{Zn}(\text{PhMe}_2\text{As})\text{Cl}_2$ . Anhydrous zinc chloride (1 mol.) was warmed in acetone and phenyl dimethyl arsine (1 mol.) added, and the solution concentrated to a syrup on the water bath. It was then placed in a vacuum desiccator and allowed to stand. Colourless needles separated after four days. These were removed and washed with ether. The same compound was obtained even when a large excess of the arsine was used. The melting point was indefinite, the crystals beginning to soften at  $65^\circ \text{C}$ . and melting completely at about  $100^\circ \text{C}$ .

Found :  $\text{Zn}=20.8$ ,  $\text{Cl}=22.6$  per cent.

$\text{C}_8\text{H}_{11}\text{AsZnCl}_2$  requires  $\text{Zn}=20.6$ ,  $\text{Cl}=22.4$  per cent.

*Bis-phenyl dimethyl arsine zinc bromide*,  $(\text{PhMe}_2\text{As})_2\text{ZnBr}_2$ , was prepared from zinc bromide (1 mol.) and the arsine (2 mols.) in either acetone or alcoholic solution. The solution in either case was concentrated to a syrup and allowed to stand in a desiccator. Crystals separated after twelve hours, and these were washed with ether, and after recrystallisation from acetone were found to melt at  $67^\circ \text{C}$ . The same compound was obtained when one molecule of zinc bromide was treated with one of the arsine.

Found :  $\text{Zn}=11.0$ ,  $\text{Br}=27.4$  per cent.

$\text{C}_{16}\text{H}_{22}\text{As}_2\text{ZnBr}_2$  requires  $\text{Zn}=11.1$ ,  $\text{Br}=27.3$  per cent.

*Bis-phenyl dimethyl arsine zinc iodide*,  $(\text{PhMe}_2\text{As})_2\text{ZnI}_2$ , separated in colourless octahedra from a concentrated alcoholic solution of zinc iodide (1 mol.) and phenyl dimethyl arsine (2 mols.). After washing with ether and recrystallising from alcohol the compound melted at  $92^\circ \text{C}$ .

Found :  $\text{Zn}=9.6$ ,  $\text{I}=38.0$  per cent.

$\text{C}_{16}\text{H}_{22}\text{As}_2\text{ZnI}_2$  requires  $\text{Zn}=9.6$ ,  $\text{I}=37.3$  per cent.

*Bis-diphenyl methyl arsine zinc iodide*,  $(\text{Ph}_2\text{MeAs})_2\text{ZnI}_2$ , separated after three days in the form of clusters of prisms from a concentrated alcoholic solution of zinc iodide (1 mol.) and diphenyl methyl arsine (2 mols.). After washing with ether the compound was found to melt at  $128^\circ \text{C}$ . It

always had a strong odour of the arsine, even after washing with ether.

Found : I=31.1 per cent.

$C_{26}H_{26}As_2ZnI_2$  requires I=31.4 per cent.

*Bis-diphenyl methyl arsine bromide*,  $(Ph_2MeAs)_2ZnBr_2$ , separated in colourless rosettes from a concentrated acetone solution of zinc bromide (1 mol.) and diphenyl methyl arsine (2 mols.) after standing in a desiccator for two weeks. The crystals were washed with acetone and ether and were found to melt at 76° C. The compound is deliquescent.

Found : Br=22.8 per cent.

$C_{26}H_{26}As_2ZnBr_2$  requires Br=22.5 per cent.

*Bis-o-tolyl dimethyl arsine zinc iodide*,  $(o-C_7H_7Me_2As)_2ZnI_2$ , separated after three days in short colourless prisms from a concentrated solution of the arsine and zinc iodide in absolute alcohol. After washing with ether the compound was found to melt at 121° C.

Found : I=39.0 per cent.

$C_{18}H_{26}As_2ZnI_2$  requires I=39.0 per cent.

*Bis-p-tolyl dimethyl arsine zinc iodide*,  $(p-C_7H_7Me_2As)_2ZnI_2$ , prepared like the previous compound from *p*-tolyl dimethyl arsine and zinc iodide, after washing with acetone was found to melt at 115° C.

Found : I=38.6 per cent.

$C_{18}H_{26}As_2ZnI_2$  requires I=39.0 per cent.

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## THE CAUSES OF ICE AGES.

By GERALD H. HALLIGAN, F.G.S.

*(Manuscript received, May 20, 1936. Read, August 5, 1936.)*

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## INTRODUCTION.

Our present geological knowledge reveals the fact that during at least five, and possibly six geological periods, the climate of the earth was vastly different from that we are now experiencing.

On both hemispheres we see striations, moraines, perched blocks, etc., which could not have been caused by any action we know of but moving ice, and, as the direction of flow and the approximate thickness of the glaciers necessary to striate the hardest rocks can be traced for thousands of miles in both hemispheres, we naturally

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conclude that such conditions could occur only during periods of intense cold over the areas affected.<sup>(1)</sup>

The geological periods referred to are :

Pre-Cambrian (Proterozoic) (proved).

Lower Cambrian (proved).

Siluro-Devonian (proved).

Permo-Carboniferous (proved).

Upper Cretaceous (doubtful).

Pleistocene (proved).

Before we begin to review or criticise the theories and hypotheses referred to in this paper, it will perhaps be useful to enumerate the main fundamental facts which must be remembered by any propounder of a theory, on a subject so vast, so complicated, and so difficult, as the causes which led up to Glacial Epochs or Ice Ages.

The facts we are mostly concerned with in this discussion are :

1. Geological.
2. Astronomical.
3. Oceanographical.
4. Physical.
5. Geographical.
6. Meteorological.

## FUNDAMENTAL GEOLOGICAL FACTS.

### (a) Interglacial Periods.

Abundant evidence is now available to show that between the times of extreme cold, during each ice age, warmer periods were intercalated, during which the ice was melted, and the flora and fauna of temperate and even sub-tropical climates existed.

Perhaps the best evidence we have of inter-glacial periods is the occurrence of coal seams in polar regions now covered with ice and snow, in lat. 85° south. It is the generally accepted opinion of both geologists and palæobotanists that the flora of the coal period does not indicate the existence of a tropical, but rather that of a moist, equable, and warm-temperate climate, such as that in which we now find the most luxuriant growth of those plants of which coal is formed. These conditions are now found between latitude 30° and 40°, or about 48° nearer the equator than the Antarctic seams above mentioned. A generalised section of the seams referred to is given by Professor T. W. E. David and R. E. Priestley.<sup>(2)</sup>

Coal seams have been found in Arctic regions by V. Stefansson,<sup>(3)</sup> who states that coal, both abundant and good, was found 800 miles north of the Arctic Circle (lat. 79° N.).

Ludwig Mecking (<sup>(3)</sup>, p. 149) refers to coal of the Carboniferous, Jurassic and Tertiary periods at Ice Fiord and Bell Sound in latitude 78° N. The quality is reported to be excellent, and approximating true anthracite in appearance and chemical composition.

For further proofs of warm inter-glacial periods the reader is referred to "Climate and Time", by Dr. J. J. Croll, Chapters XV, XVI and XVII, and also to "Island Life", by A. R. Wallace, 1880, Chapter XII, pp. 114-120, where the subject is exhaustively treated.

#### (b) Glacial Records in Tropical Regions.

A very complete account of glaciation of Triassic or Triassic-Jurassic age is given by Ball and Shaler<sup>(4)</sup> from Lualaba Valley, west of Lake Tanganyika, Central Africa, in lat. 3° 30' to 5° south. The glacial materials come from the south and extend for about 100 miles.<sup>(5)</sup>

The northern edge of known ice action in Carboniferous times in Africa is latitude 23° S. in Madagascar and 22° in the Union. It extends from sea to sea, and the striae run S. or S.W. over the whole area.<sup>(6)</sup>

The glacial deposit in the Talchirs of Central India in lat. 19° 53' N. near the little village of Irai, on the Penganga River, at an elevation of less than 900 feet above sea-level, is the nearest to the equator of any known ice action in the northern hemisphere. It reaches lat. 17° 20' N. and extends northwards to lat. 24°, a distance of nearly 500 miles (<sup>(5)</sup>, p. 100, (<sup>7</sup>), pp. 22-23).

The Salt Range boulder clays of North-west India are situated in lat. 32½° N. and long. 72½° E. All the ordinary features of glacial deposits are shown in the Salt Range tillites, with one unusual feature. Sometimes the striated pebbles are sharply faceted, as if they had been held firmly in one position till a smooth face was ground, and then shifted till another was made. Some of the boulders of the Salt Range tillites are of rocks whose only known source is about 750 miles (11° of latitude) to the south, which means that the glacier advanced from the south to north instead of in the reverse direction as one would expect.

In Australia we have undoubted evidence of the equatorward limit of the Kamilaroi (Permo-Carboniferous) glaciation having come to sea-level as far north as latitude  $18^{\circ}$  South, long.  $124^{\circ}$  East.<sup>(8)</sup>

From the fundamental geological facts here stated, we now see that a moist, equable and warm-temperate climate, favourable to the growth of plants such as *Lepidodendron*, *Sigillaria* and other trees of which coal is almost wholly composed, has existed in latitude  $85^{\circ}$  South, and in latitude  $79^{\circ}$  North. On the other hand, we find undoubted evidence of glacial action in latitude  $3\frac{1}{2}^{\circ}$  South in Central Africa, in latitude  $17^{\circ} 20'$  North in Central India, and in latitude  $18^{\circ}$  South in Australia.

#### FUNDAMENTAL ASTRONOMICAL FACTS.

The astronomical facts which have any connection with the past changes of climate of the earth may be divided into three parts: (a) the obliquity of the ecliptic, (b) the longitude of the perihelion, and (c) the eccentricity of the earth's orbit.

##### (a) The Obliquity of the Ecliptic.

We know that the present mean value of the obliquity of the ecliptic is  $23^{\circ} 27'$ , and we have it on the authority of Laplace,<sup>(9)</sup> Stockwell<sup>(10)</sup> and others that the greatest and least declinations of the sun at the solstices can never differ from each other to any greater extent than  $2^{\circ} 27' 22''$ , its present obliquity being  $23^{\circ} 27' 30''$ . This small variation would affect the climate of the temperate and tropical regions to a very slight extent, but at the polar regions the effect would be greater. From these facts we know that these differences are not sufficient to cause an ice age, and, further, that no possible change in the amount of the obliquity could appreciably affect the climate. They must, however, be borne in mind when considering other facts in connection with glacial epochs.

The tropical year, or the apparent time of the sun's circuit of the heavens, is 20.1 minutes shorter than the earth's revolution period; in other words, if the sun starts from that point of the ecliptic known as the vernal equinox, it will reach it again 20.1 minutes before completing the annual circuit of the heavens.

Thus the equinox seems to be slowly moving along the ecliptic to meet the sun, and so every year it precedes, or

comes before its former position, the phenomenon being known as the Precession of the Equinoxes. By the effect of precession, both the line of equinoxes and those of the solstices retreat on the ecliptic by an annual angular movement of  $50'' \cdot 1$ , which cause would carry them round, with respect to the axis of the earth's ellipse, through a complete revolution in 25,868 years. In this period, assuming the axis to retain a fixed position, the perihelion would come to coincide successively in longitude with both the solstices, and with both the equinoxes. The axis, however, does not remain so fixed, but shifts its position with a much slower angular movement of  $11 \cdot 8''$  per annum in the opposite direction to that in which precession carries the line of equinoxes, by which movement alone, if uniformly continued, the direction of the axis itself would be carried entirely round the circumference of the ecliptic in 109,830 years. In consequence of this joint variation, then, the place of the perihelion must coincide with the vernal equinox, at intervals of about 10,500 years, during which period the extreme summer and winter of one hemisphere will have been transferred to the other.<sup>(11)</sup>

#### (b) The Longitude of the Perihelion.

If the rate of precession and the motion of the perihelion were always uniform, the periods would all be the same length, but, although the rate of precession is not subject to much variation, such is not the case in regard to the motion of the perihelion, which is sometimes rapid and at other times slow, while in some cases its motion is retrograde. In consequence of this the glacial or the interglacial periods of a glacial epoch may not be more than some six or seven thousand years in length, while in other cases their length may be as much as fifteen or sixteen thousand years.<sup>(12)</sup>

#### (c) The Eccentricity of the Earth's Orbit.

We know that the orbit of the earth is elliptical, and that the eccentricity varies from almost a circle to 0.069 (Stockwell,<sup>(10)</sup> p. xi). When the eccentricity is at its superior limit the distance of the sun from the earth, when the latter is in aphelion of its orbit, is no less than 98,506,350 miles, and when in the perihelion it is only 84,293,650 miles; thus it is 14,212,700 miles further from the sun in the former position than in the latter. The direct heat of the sun being inversely as the square of

the distance, it follows that the amount of heat received by the earth when in these two positions respectively will be as 19 to 26. Taking the present eccentricity to be 0.0168, the earth's distance during winter in the northern hemisphere, when in perihelion, is 89,864,480 miles. Suppose now that, owing to precession, winter in the northern hemisphere should happen when the earth is in the aphelion of its orbit, at the time when the orbit is at its greatest eccentricity; the earth would then be 8,601,870 miles further from the sun in winter than at present. The direct heat of the sun would therefore be one-fifth less during the winter than at present; and in summer one-fifth greater. These large differences would certainly affect the climate to a very great extent. In this case the difference between summer and winter in the latitude of England would be almost annihilated.

"But as the winter in one hemisphere corresponds to summer in the other, it follows that while one hemisphere would be suffering the greatest extremes of summer-heat and winter-cold, the other would be enduring a perpetual summer" <sup>(12)</sup>, p. 56).

From the facts thus far enumerated we must conclude that, even when the longitude of the perihelion is  $0^\circ$ , at a time of maximum eccentricity of the earth's orbit, it does not follow that a glacial epoch will result. Rather may it be said that the conditions tend to produce glacial conditions upon one hemisphere and genial to hot conditions on the other.

So far we have been treating of matters which may be dealt with on purely mathematical grounds. The occurrence of the seasons, due to the obliquity of the ecliptic, the precession of the equinoxes, which causes the winter solstice, occurring when the earth is in perihelion, to be brought round to aphelion at intervals averaging about 10,500 years, the eccentricity of the earth's orbit, which causes a very much greater amount of sun-heat to be received in the hemisphere which happens to be nearest the sun when the earth is in perihelion, are all well known and undoubted astronomical facts.

When we come to consider the combined influence of a multitude of physical causes, depending on many different elements, some of which are not well understood, we are compelled to fall back on logical analysis, rather than on mathematics, notwithstanding our natural predilection for rigid mathematical investigation.

## FUNDAMENTAL PHYSICAL FACTS.

## (a) Trade-Winds.

It is obvious that the strength of the trade-winds depends upon the difference in temperature that may exist between the thermal equator and higher latitudes, so that should the sun always be directly above the equator, there would be no difference between the strength of the trade-winds in either hemisphere. But as the eccentricity of the earth's orbit increases, that hemisphere, say the northern, which has its winter season when the earth is in perihelion, will be colder than the other hemisphere, with a consequent increase in the strength of its trade-winds. In other words the median line between the trades will lie to a very considerable distance to the north of the equator. At the present time the difference of temperature between the two hemispheres is less than it would be were the eccentricity anywhere near its maximum, yet we find the south-east trades blow with greater force than the north-east, and sometimes extend to latitude  $10^{\circ}$  or  $15^{\circ}$  North, whereas the north-east trades rarely blow south of the equator.<sup>(12) (13) (14)</sup>

## (b) The Causes of Ocean Currents.

The prevailing winds of the globe undoubtedly originate and maintain the *surface* currents of the ocean, but sometimes the influence of these currents is, through friction, felt to a depth of many fathoms. This statement is liable to cause much confusion unless it is made perfectly clear that it is the *surface* currents only that are originated by wind action.

As the movements of ocean water play such a very important part in the discussion of the causes of an ice age, I would like to call attention to some of the most intricate aspects of this complex question.

There are many sub-surface currents, some of them being horizontal and some vertical, and most of them are deflected when they impinge upon shoals, or upon meeting with sudden deeps, or when they encounter other currents of a different salinity, density, or temperature. We must also consider the up-welling of cold water over an enormous area on the western sides of all continents, which has considerable effect upon climate. This phenomenon is caused in the following way.

The western shores of the continents are the weather shores of the oceans. Europe, Africa, America and Australia extend from the northern trade-wind region, through the equatorial calms, to the southern trade-wind region, and as the trade-winds blow from the north-east and the south-east, the result of their mechanical action is to drag away the water from their weather shores and drive it to leeward.

The surface water (which assumes the temperature due to the local climate) is thus removed, and is replaced by the up-welling of the deeper layers. But in low latitudes, the deeper water in the ocean has always a very much lower temperature than the surface water, hence at the weather shores (the western shores) of the oceans we have a constant removal of the surface water to leeward, and replacement of it by colder water from greater depths. But the current which brings the cold water there is not a horizontal current from higher latitudes, but a vertical one from greater depths, and this cannot be due to any wind action.

In all latitudes we find almost ice-cold water at a few hundred fathoms from the surface, and in fact the nearer we come to the equator the nearer does the cold water come to the surface. In latitude  $5^{\circ} 5'$  South (at Payta in South America), and away from the coast, water at  $60^{\circ}$  Fah. would naturally be found at a depth of about 100 fathoms; at the surface, in the open ocean, it would not be found at a less distance than 2,000 miles. A similar phenomenon is observed on the western coasts of Africa and Australia, and on the Californian coast of Western America <sup>(15)</sup>, <sup>(13)</sup>, p. 69, <sup>(12)</sup>, p. 15 *et seq.*

Many other instances might be quoted to show that cold water is brought to the surface in low latitudes over many thousands of square miles, and thus has a very considerable influence upon the climate of the globe. It must of course be admitted that wind action is *indirectly* the cause of the up-welling, but as the winds themselves are wholly due to difference of atmospheric temperature, and these in turn are the result of the varying amount of sun-heat received at different latitudes, we must go back to the primary cause in order to account for the oceanic circulation. It seems best to say that the winds are the cause of *surface* currents, and thus avoid all confusion. We have also to consider the tidal currents, the current deflection caused by the earth's rotation, and some of the

subsidiary causes which powerfully influence oceanic circulation, and therefore climate. The subsidiary causes are: (1) abnormally heavy rainfall such as occurs in the West Pacific, (2) under currents of high temperature and density from the Mediterranean and Red Sea, (3) the inter-tropical position of the line of lowest mean barometric pressure, resulting in a temperature much higher in the North Atlantic than in the South Atlantic, and much higher in the South Pacific than in the North Pacific.

But there is yet another phenomenon connected with ocean currents which confronts the oceanographer and which makes the problem still more complex. In comparatively recent years it has been found that the rise and fall of the tide is accompanied by currents, especially where obstructions are met with, and the height to which a tide will rise is determined by land configuration. Tidal currents prevent the formation of muddy deposits on the top of the Wyville Thomson Ridge at a depth of 250 fathoms. J. Y. Buchanan measured tidal currents on the Dacia Bank in 1883, and R. N. Wolfenden discovered similar tidal currents on the Gettysberg Bank. More recently the "Michael Sars" expedition of 1910 measured tidal currents in the open ocean to a depth of 400 fathoms.<sup>(15)</sup> It is more than probable that the whole of the ocean water is subjected to tidal stress, and the consequent movement must deflect, accelerate or retard the other currents of the ocean, though the amount of the interference is at present a matter of conjecture.

In short, the unknown elements in the problem of oceanic circulation, even under the present almost ideal conditions, are so many that it becomes one of insoluble complexity.

Dr. J. J. Croll<sup>(12) (13)</sup> realised our imperfect insight into the laws which govern meteorological and physical phenomena, and was content to discover the expression of a general law under the disguise of ever varying and often apparently contradictory appearances.

#### (c) Action and Reaction of Physical Agents.

One of the greatest difficulties in the path of the general reader of ice age theories is that of the absorption and dissipation of heat rays by land and water, by fogs and clouds, and by gases, but especially by aqueous vapour, which acts so very differently under different conditions. Another stumbling block is the mutual action and reaction of the physical agents brought into action by changes



in atmospheric and oceanic currents. So far as I am aware, no author has dealt so exhaustively with both of these important subjects—vital to the question at issue—as Dr. J. J. Croll, but notwithstanding Croll's lucid explanations, he has been repeatedly misquoted and misunderstood by many writers. The full text of his clear exposition would perhaps be too long for this paper, especially as the reference given is so readily available, but the matter is of sufficient importance to justify the following brief synopsis.

The diathermancy of air has been well established by the researches of Professor Tyndall on radiant heat. Perfectly dry air is nearly incapable of absorbing radiant heat; the entire radiation passes through it almost without any sensible absorption. Air is cooled by contact with snow-covered ground, but is not heated by radiation from the sun. No matter what the intensity of the sun's rays may be, the temperature of snow and ice can never rise above 32° Fahr. Hence the presence of snow and ice tends by direct radiation to lower the temperature of all surrounding bodies to 32° Fahr. Air charged with aqueous vapour is a good absorber of radiant heat, but it can absorb only those rays which agree with it in *period*, and it so happens that rays from snow and ice are those which it absorbs best. The humid air will absorb the total radiation from the snow and ice, but it will allow the greater part of, if not nearly all, the sun's rays to pass unabsorbed. But during the day, when the sun is shining, the radiation from the snow and ice to the air is negative; that is, the snow and ice cool the air by radiation. The result is that the air is cooled by radiation to the snow and ice more rapidly than it is heated by the sun; and, as a consequence, in a country covered mostly with an icy mantle, the temperature of the air, even during summer, seldom rises above freezing point.

Snow is a good reflector, but as reflection does not change the character of the rays, they would not be absorbed by the air, but would pass into stellar space. A good many of the writers on ice age matters seem to be confirmed in the idea that the quantity of snow and ice melted must be proportional to the amount of sun-heat received, but this assumption is totally opposed to known facts. We know that there is no place on the face of the globe where the amount of heat received from the sun is not far more than sufficient to melt all the snow which

falls upon it, so that if it were true that the amount of snow melted is proportional to the amount of heat received by the snow, then there could be no such thing as perpetual snow.

#### FUNDAMENTAL OCEANOGRAPHICAL FACTS.

It is important to note that land configuration plays an important part in modifying both the direction and velocity of atmospheric and oceanic currents. Every terrestrial area, both on land and sea, has its own system of atmospheric and oceanic currents; as every part of a continent and every valley has its own climate, subject to the general laws which govern the circulation of currents and the distribution of climate over the whole of our planet.

It is these general laws we have to consider when dealing with the world-wide phenomenon of the causes of an ice age. We know a good deal of the complex sensations of heat and cold, of the movements of such fluids as water and air, and their action and reaction under the conditions now existing on the globe, but when such cosmic changes take place as lead to a complete change of conditions, it becomes difficult if not impossible to correlate cause and effect, and to visualise the enormous transformation brought about by ever varying and often contradictory phenomena.

It is difficult to write an epitome of our knowledge of the circulation of oceanic water, even under existing conditions, which permit access to thousands of records, specially tabulated and most carefully analysed. Perhaps the following summing up of the fundamental facts of the subject, which I quote from "*Thalassa*", by J. J. Wild, page 45 *et seq.*, will make the matter clear.

"It may be taken for granted that, water being a ponderable substance, and as such subject to the laws of gravity, the different strata of the ocean will be found arranged according to weight, the heavier strata below, the lighter strata above.

"The weight of salt water varies with two conditions: temperature and percentage of salt held in solution. In the tropical belt the surface stratum contains more salt, the increase being due to evaporation, caused by the rays of the sun. In polar regions the quantity of salt falls below the average on account of the greater proportion of fresh water from the melting of the ice, and from precipitation.

"According to the extensive series of specific-gravity observations on sea water, made on board H.M.S. *Challenger* by J. Y. Buchanan, it appears that the specific gravity of salt water under the influence of temperature, varies between a minimum of 1.021 and a maximum

of 1.028 (to use round numbers), and the specific gravity as affected by the percentage of salt contained in the water, between 1.024 and 1.027 . . . . It will thus be seen that the difference in specific gravity due to temperature is more than double that due to the varying percentage of salt; whence we conclude that the order of the oceanic strata depends, in the first instance, upon temperature, in the second upon the amount of salt held in solution.

"An equatorial surface-current will remain such so long as the temperature is sufficiently high to render it lighter than the surrounding waters, but as during its progress towards higher latitudes its temperature decreases, it will, on account of its greater saltiness, sink below the fresher water of these latitudes and continue its course as a warm under-current towards the polar regions. On the other hand a polar surface-current, although composed of fresher water, will, on arriving at a certain latitude, sink below the tropical waters on account of its low temperature, and consequent greater specific gravity, and continue its course towards the equator as a cold under-current.

"But the temperature of the ocean decreases not only from the Equator towards the Poles, but also from the surface towards the bottom. Hence in the tropical regions the warm but salt surface water will sink on becoming cooled by its contact with the strata beneath, and impart some of its heat to the latter; while in the polar regions the fresh, but cold surface water, produced by the melting of the ice will, on becoming more salt by its admixture with the surrounding water, sink in its turn, and lower the temperature of the strata with which it comes in contact.

"The final result of these exchanges of temperature, which constitute what may be called the vertical circulation of the oceanic waters, appears in the oblique position, and the consequent spreading out of the isotherms as we recede from the Equator. The isotherm of 41° Fahr. (5° Cent.), for example, which, near the Equator, is found at a depth of 300 fathoms, is met with at 600 fathoms in lat. 50° S. in the Southern Ocean, and at 800 fathoms in lat. 50° N. in the North Atlantic."

This masterly epitome enables us to envisage the extraordinarily complicated nature of the circulation of ocean water under the most simple conditions possible, that is, at a time when the earth's orbit round the sun is very nearly a circle, and the average temperature of both hemispheres is practically the same.<sup>(12) (13) (15)</sup>

We have already seen (see Fundamental Astronomical Facts. (c) The Eccentricity of the Earth's Orbit, p. 229) that when the eccentricity of the earth's orbit is at its superior limit, the earth is fourteen million miles nearer to the sun when in perihelion than in aphelion, and consequently the amount of heat received when in these two positions will be as 19 to 26.

One result of this enormous difference would certainly be to change the position, the direction of flow, and the velocity of every atmospheric and oceanic current, both surface and sub-surface, and thus to effect a complete change of the climate of the globe.

After more than fifty years of practical hydrographic and meteorological study, I still find it impossible to produce an accurate ocean current chart of the world, or even of one ocean, under the changed conditions stated above.

We know, however, the proportion of warm water that will be diverted from one hemisphere to the other, and also the general trend of the main oceanic currents, under the changed conditions, and thus may deduce, with some confidence, the climatic effects of such changes. But the one important fact to be remembered by all writers who seek the causes of ice ages, by propounding either theories or hypotheses, is that these vast changes in climatic conditions do take place owing to the physical changes due to cosmic causes which are well understood and cannot be questioned.<sup>(14) (17)</sup>

#### FUNDAMENTAL GEOGRAPHICAL FACTS.

The geographical facts which must be considered in connection with ice ages consist of the configuration of land and water, the elevations and depressions in the sea bottom, and the contour of the sea coast. The geographical conditions cannot properly be said to be causes, in the sense in which the astronomical and physical are. They are more properly *conditions* in the production of a glacial epoch, in that they influence the direction of flow and the velocity of ocean currents. In one respect we may say that the astronomical causes produce glaciation by means of the physical agencies, which can be effective only when the geographical conditions are favourable.<sup>(13) (15)</sup>

It must here be stated that all calculations and assumptions are based upon the supposition that the geographical conditions, at least as far back as Silurian time, were not essentially different from those which now obtain.<sup>(13)</sup> In fact we accept this as our one great geographical fact, seeing that we have no evidence to show that it was ever otherwise.

We see from this that comparatively small geographical changes, such as a subsidence of Central America between lat. 20° and 8° North, or an elevation of the well known ridge extending from the Shetland Islands through the Faroes and Iceland to Greenland, in the North Atlantic, or of the Behring Strait would considerably modify a glacial epoch by changing the oceanic circulation.

We know that such minor changes in land configuration, both above and below sea-level, have always taken and

are still taking place. But there is no geological evidence to show that, at least since Silurian times, the Atlantic and Pacific were ever, in their broad features, otherwise than they are now.

### FUNDAMENTAL METEOROLOGICAL FACTS.

#### (a) Trade-Winds.

The origin of the trade-winds, as already stated, is the great difference between the air temperature at the equator and at the poles, which causes a constant flow of air towards the equator. When the eccentricity of the earth's orbit is at a high value, and the northern winter solstice is in perihelion, it necessarily follows that the medial line of the trade-winds is shifted to the north, and consequently the south-east trade-winds are stronger than the north-east, and blow over upon the northern hemisphere, as far probably as the Tropic of Cancer. The result is that all the great equatorial currents of the ocean are impelled into the northern hemisphere, which thus, in consequence of the immense accumulation of warm water, has its temperature raised and snow and ice to a great extent must then disappear from the Arctic regions. When the precession of the equinoxes brings round the winter solstice to aphelion the condition of things on the two hemispheres is reversed, and the north-east trades then blow over upon the southern hemisphere, carrying the great equatorial currents along with them. The warm water being thus withdrawn from the northern hemisphere, its temperature sinks enormously, and snow and ice begin to accumulate in temperate regions. The amount of precipitation in the form of snow in temperate regions is at the same time much increased by the excess of evaporation in low latitudes, resulting from the nearness of the sun in perihelion during summer. <sup>(13)</sup> <sup>(14)</sup>

Speaking broadly, the above statement represents one of the most important facts which must be considered when dealing with the causes which led to ice ages.

#### (b) Atmospheric Circulation.

In the report on the scientific results of the Challenger Expedition, A. Buchan<sup>(15)</sup> concluded his discussion of the atmospheric circulation as follows :

"The isobaric maps show, in the clearest and most conclusive manner, that the distribution of the pressure of the earth's atmosphere

is determined by the geographical distribution of land and water in their relations to the varying heat of the sun through the months of the year; and since the relative pressure determines the direction and force of the prevailing winds, and these in turn the temperature, moisture, rainfall and, in a very great degree, the surface currents of the ocean, it is evident that there is here a principle applicable not merely to the present state of the earth, but also to different distributions of land and water in past times."

A detailed explanation of the phenomenon of atmospheric circulation involves many complex problems, but the main features may be epitomised thus:

The dominant winds on the earth fall into three groups. One-half of the earth's surface—between lat.  $30^{\circ}$  N. and  $30^{\circ}$  S.—is controlled by the trade winds which blow equatorward. The remaining portions are chiefly affected by westerly and south-westerly winds. At the south and at the north pole the winds are necessarily equatorward also. Hence the return poleward winds which complete the circulation must be confined to cold regions above the earth, of which we have not such detailed knowledge.<sup>(20)</sup> From this terse and lucid definition, which is undoubtedly consonant with all known facts, we see that *no heat can be transported to temperate or polar regions by winds.*

We know of course that heat is conveyed to temperate and polar regions, and it seemed natural to conclude that air was the means of conveyance. It was not till the year 1864 that Dr. J. J. Croll wrote his paper "On the Physical Cause of the Change of Climate during Geological Epochs" in the *Philosophical Magazine* of August, 1864, in which he showed that the ocean currents were the transporters of heat from the tropics to the polar regions, and also the transporters of cold from the polar regions to the tropics. Considerable support was given to the original fallacy by the report of the Siberian expedition under H. Seeböhm,<sup>(21)</sup> who describes the sudden melting of the snow in the valley of the Yenisei River in North Siberia.

In the valley of the Yenisei River in Siberia, which has its source in Savansk Mountains, about 6,000 to 7,000 feet above sea-level, in lat.  $51^{\circ}$  N., and its mouth in lat.  $69^{\circ}$  N., about six feet of snow covers the country all the winter and spring, and it is not sensibly diminished by the sun-heat so long as the northerly winds keep the air below freezing point. But early in June the wind changes to a warm southerly, and under its influence the snow disappears in a few days and a luxuriant vegetation appears. This warm southerly wind is always referred to as the anti-

trade-wind coming from the equator, about 2,000 miles away, and still retaining enough heat to melt six feet of snow in a few days, notwithstanding that it has been blowing above the snow-line for the whole distance. It is therefore assumed by most, if not all meteorologists, that the anti-trade-winds must carry an enormous amount of heat to the poles, and thus decrease the severity of a glacial epoch. The southerly wind here referred to is certainly a continuation of the so-called anti-trade-wind, the temperature of which when it arrived at the Savansk Mountains cannot have been more than 32° Fahr. It here meets the updraft northerly winds, and is deflected downwards to the valley of the Yenisei and other rivers.

Now, when cold air from a great altitude is carried towards the earth's surface by a descending current, the pressure upon it is continually increasing, and its volume is being reduced. The work thus done on the air by gravity is changed into heat, in accordance with Boyle's law, and the temperature of the air rises about 1° Fahr. for each 180 feet it descends.\* It will thus be clear that the temperature of the air when it reaches the sea-level in the valley will be about 72° Fahr.—quite warm enough quickly to melt the snow, as described by H. Seeböhm. In Siberia these warm winds last for a few weeks only, and their effect upon the climate must be regarded as local, and therefore negligible, when dealing with such world-wide questions as the "causes of an ice age". Similar warm dry winds are called the föhn in the Eastern Alps, and the chinook in the great plains of Canada. They owe their warmth to the thermodynamic heating of the air which has blown over high ground and precipitated most of its water vapour.

In the foregoing few pages I have endeavoured to state the main fundamental facts which must be adhered to when propounding any theory or hypothesis to account for those vast secular changes of climate called glacial epochs. There are, of course, many other facts of considerable importance which will occur to my readers, but those cited are the ones most often overlooked or misunderstood by writers on this vast and complex subject.

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\* The actual rate of change of temperature in the air near the earth's surface is not so great as this, for the sun has a certain heating effect, but this would be so small as not to affect the question at issue.

THEORIES AND HYPOTHESES ON THE CAUSES OF  
GLACIAL EPOCHS.

Since the year 1864, when Professor Frankland propounded the theory that a difference in the influence of internal heat on the sea and on the land was sufficient to cause an ice age, much has been written on the subject by some of the foremost thinkers of the age, as the following brief synopsis, in approximately chronological order, will show.

1. Frankland, Professor E.: *Phil. Mag.*, 1864, 27, 321-341.  
(Difference in the influence of internal heat on the land and in the sea.)
2. Poisson, S. D.: *Compt. Rend.*, 1837, 4, 137-166.  
(The earth passed through hotter and colder regions of space.)  
For criticism of this hypothesis, see W. Hopkins, *Quart. Journ. Geol. Soc.*, 1852, 8, 56, 58, 62.
3. Lecoq, H.: *Epoques Geol. de l'Auvergne*, Vol. 4.  
(Change in the amount of sun-heat.)
4. Drayson, Lieut.-Col. W. W.: *Quart. Journ. Geol. Soc.*, 1891, 27, 232-233.  
(Change in the obliquity of the ecliptic.)
5. Lyell, Sir Charles: "Principles of Geology", 11th Edit., 1872, Vol. 1, 270.  
(Relative distribution of land and sea.)
6. Best, Thomas: *Quart. Journ. Sci.*, 1874.  
(Change in the obliquity of the ecliptic.)
7. Wallace, A. R.: "Island Life", 1880, pp. 104, *et seq.*
8. Geikie, Professor James: "Prehistoric Europe", 1881; "The Great Ice Age", 2nd Edit., 1877, 3rd Edit., 1894.
9. Geikie, Professor Archibald: "Text-book of Geology", 3rd Edit., 1893, pp. 23-30.
10. Croll, Dr. J. J.: "Climate and Time", 4th Edit., 1890; "Climate and Cosmology", 1899.
11. Høgbom, A. G.: *Svensk Kemisk Tidskrift*, 1894, 6, 169.  
(Variation in the amount of carbon dioxide in the atmosphere.)
12. Culverwell, E. P.: *Geol. Mag.*, 1895, 2, 3-13, 52-65.  
(Criticism of astronomical theory.)
13. Arrhenius, Dr. S. A.: *Phil. Mag.*, 1896, 41, 237-276.  
(Variation in the amount of carbon dioxide in the atmosphere.)
14. Chamberlin, Professor T. C.: *Journ. of Geol.*, 1897, 5; 1898, 6; 1899, 7.  
(Variation in the amount of carbon dioxide in the atmosphere.)
15. Darwin, Charles: "Origin of Species", Popular Impression, 1902, Chap. 13.
16. David, Sir T. W. E.: *Compt. Rend.*, X<sup>e</sup> Congress Geol. Internat., 1907, Vol. 1, pp. 437-482.  
(Conditions of climate at different geological periods.)
17. Taylor, T. Griffith: *Geogr. Review*, 1919, 8.  
(Retardation of earth's rotation.)
18. Spitaler, H.: "Das Klima des Eiszeitalters", Prague, 1921.
19. Brooks, C. E. P.: "The Evolution of Climate", 1922.
20. Köppen, W., and Wegener, A.: "Die Klimate der geologischen Vorzeit", Berlin, 1924.



21. Coleman, A. P.: "Ice Ages, Recent and Ancient", 1926.
22. Simpson, Dr. G. C.: "Past Climates." Alex. Pedler Lecture, British Science Guild, 1929.

The above list comprises one theory, thirteen hypotheses and eight contributions devoted to criticism only. Of the hypotheses, one is based on the influence of internal heat on the land and on the sea, four are based upon an assumed variation in the amount of heat received on the earth, two depend upon a change in the obliquity of the ecliptic, two necessitate a change in the distribution of land and sea, two require a variation in the amount of carbon dioxide in the air, one requires a retardation of the earth's rotation, and one is based upon Wegener's hypothesis of continental displacement.

The one and only theory on the subject of the origin of glacial epochs was propounded by Dr. J. J. Croll in 1864,<sup>(22)</sup> and in separate papers in the *Philosophical Magazine* and other journals up to 1875, when he issued the first edition of "Climate and Time". In 1890 the fourth edition of "Climate and Time" appeared and also "Climate and Cosmology", which embodies a critical review of all the works by other writers up to that date. In order to make this paper more complete I now include a short review of these papers, based, in some cases, upon more up to date information.

## *No. 2. The Earth Passed through Hotter and Colder Parts of Space.*

There is no doubt a difference in the quantity of force in the form of heat, passing through different parts of space; but space itself is not a substance which can be either cold or hot, so that if we are to adopt this hypothesis we must assume that the earth, during the hot periods, must have been in the vicinity of some other source of light and heat besides the sun. A mass of such magnitude as would be sufficient to affect the earth's climate to any great extent would by its gravity seriously disarrange the mechanism of our solar system, and certainly the orbits of the planets would at the present day afford some evidence of it. Again, in order to account for a cold period, such as the glacial period, we must assume that the earth must have come into the vicinity of a cold body, but all the information we possess in regard to interglacial periods is wholly irreconcilable with this hypothesis.<sup>(23)</sup>

Nos. 3, 19 and 22. *Variation in the Amount of Sun-heat Received on the Earth.*

The theory that the sun is a variable star, and that the glacial epochs of the geologists may correspond to periods of decrease in the sun's heat, was propounded by H. Lecoq. It is open to two fatal objections : (1) a general diminution of heat can never produce a glacial epoch, and (2) even if it could, it would not explain interglacial periods,<sup>(28)</sup> and thus fails to comply with Fundamental Geological Fact No. 1. It must be remembered that snow can only result from heat which causes evaporation, and cold which causes condensation. It therefore follows that the less heat received on the earth the less snow, and the less snow the smaller the glaciers, and this of course is the very opposite to what is required to cause an ice age or glacial epoch.

Dr. G. C. Simpson,<sup>(24)</sup> when discussing the effect on a polar climate of changes in solar radiation, says : " There is strong independent support of the conclusion that an increase of solar radiation would increase the glaciation of the region we are considering. This, however, would only be the initial effect of increasing the radiation ; if the increase progresses there will come a time when the increased temperature produces melting in the summer. From this point on, melting becomes more and more important, until finally the annual melting might be as great as the annual snowfall, when the ice covering would disappear." Dr. Simpson has forgotten that, no matter what the intensity of the sun's rays may be, the temperature of snow and ice can never rise above 32° Fahr. Hence the presence of snow and ice tends, by direct radiation, to lower the temperature of all surrounding bodies to 32° Fahr. The diathermancy of air has been well established by the researches of Professor Tyndall<sup>(12)</sup>, pp. 410-411) on radiant heat, and the conclusion arrived at is that the air is cooled by *contact* with the snow-covered ground, but is not heated by the radiation from the sun.

Snow and ice lower the temperature by chilling the air and condensing the vapour into thick fogs. The increased strength of the sun's rays during summer, owing to his nearness at that season, would, in the first place, tend to increased amount of evaporation, but the presence of snow-clad mountains and an icy sea would chill the air and condense the vapour into fogs. The thick fogs and cloudy sky would effectually prevent the sun's rays from

reaching the earth, and the snow, in consequence, would remain unmelted during the whole summer. There are many examples of this condition of affairs on some of the islands in the Southern Ocean at the present day. Sandwich Land, which is in the same parallel of latitude as the north of Scotland, is covered with ice and snow during the entire summer; and in the island of South Georgia, which is in the same latitude as the centre of England, the perpetual snow descends to the sea beach. At Admiralty Inlet, South Shetlands, in lat.  $64^{\circ}$ , there is perpetual snow, and the thermometer records  $23^{\circ}$  Fahr. in the middle of summer.

From this it will be seen that Dr. Simpson's assumptions on the melting of snow in the polar regions, owing to increased radiation, are not borne out by observed facts.

*Nos. 4 and 6. Variation in the Obliquity of the Ecliptic.*

Lieut.-Col. Drayson in 1871, and Mr. Thos. Belt in 1874, brought forward the hypothesis that, should the obliquity increase from its present value of  $23^{\circ} 27\frac{1}{2}'$  to about  $35^{\circ}$  or more, the Arctic Circle would be brought down to latitude  $54^{\circ} 34' 13''$ , which is about the latitude of England, thus bringing about a condition of climate similar to that in the Arctic regions. Sir Charles Lyell also refers to the influence of a reduced obliquity of the ecliptic on climate.<sup>(25)</sup> It has already been shown (see Fundamental Astronomical Facts (a) The Obliquity of the Ecliptic) that even if the obliquity increased to its possible limit, as determined by Laplace,<sup>(9)</sup> Stockwell<sup>(10)</sup> and others, it could not appreciably affect the climate of the globe, so that this hypothesis must also be ruled out.

*Nos. 5 and 20. Relative Distribution of Land and Sea.*

In the year 1872 Sir Chas. Lyell<sup>(25)</sup> advanced the hypothesis that if all the land were collected round the poles, while the remainder of the globe were occupied by the ocean, the general temperature would be so lowered that a glacial epoch would result. On the other hand, were all the land collected along the equator, and the polar regions covered with sea, the temperature of the globe would be enormously increased. In reply to these statements Dr. Croll<sup>(12)</sup>, Chaps. 2-3 and p. 9) has pointed out that in order to raise the mean temperature of the whole earth, *water* should be placed along the equator, and not *land* as Sir Chas. Lyell and others have supposed.

If all the land is placed along the equator the possibility of conveying the sun's heat from equatorial regions by means of ocean currents is prevented, and the transfer of heat could then be effected only by means of the upper currents of the trades, and we have seen by Fundamental Physical Fact (a) that heat is not conveyed by this means.

The ground surface at the equator becomes intensely heated by the sun's rays, and radiates its heat more rapidly into space than from a surface of water heated under similar conditions, and consequently the ascending current of air carries off a greater amount of heat. If the heat thus carried away were transferred by means of upper currents to higher latitudes, and thus employed to warm the earth, it might to a considerable extent compensate for the absence of ocean currents; but such is not the case, for the heat carried up by the ascending currents becomes less and less as it ascends, and by far the greater part of it is dissipated in the cold stellar space above. This ascending current is in reality one of the most effective means that the earth has of getting rid of the heat from the sun, and thus maintaining a much lower temperature than it would otherwise possess.

"It is in the equatorial regions that the earth loses as well as gains the greater part of its heat; so that, of all places, here ought to be placed the substance best adapted for preventing the dissipation of the earth's heat into space. Water, of all substances in nature, seems to possess this quality to the greatest extent, and besides it is a very mobile fluid, and therefore adapted, by means of currents, to carry the heat received from the sun to all parts of the globe."<sup>(12)</sup>

Dr. G. C. Simpson (<sup>24</sup>, p. 13) has shown that the distribution of land and sea can have an influence on the temperature balance only by affecting the horizontal transfer of heat through the ocean currents. This is the conclusion arrived at by Dr. Croll<sup>(22)</sup> in 1864, and long since generally accepted.

*Nos. 11, 13, 14. Variation in the Amount of Carbon Dioxide in the Air.*

It has been suggested<sup>(26)</sup> that variations in the amount of carbon dioxide in the air would account for very large changes in the radiation of heat from the earth's surface, and thus account for glacial epochs. Carbon dioxide certainly allows the sun's rays to pass through unchanged, but absorbs some of the heat rays radiated from the earth, thus preventing them passing through and being lost in

space. It follows that any diminution of carbon dioxide in the air would cause the earth, at that place, to radiate its heat more readily, and so reduce its temperature. The propounders of this hypothesis overlooked the fact that terrestrial radiation which gas is capable of absorbing is taken up equally readily by water-vapour, of which there is always sufficient present, so that carbon dioxide cannot have any appreciable effect on the climate.

*No. 17. Retardation of the Earth's Rotation.*

Mr. Griffith Taylor in 1919<sup>(27)</sup> suggested "that a slight variation in the diurnal rotation of the earth would cause the circulation of the atmosphere to change in character. At present a spot on the equator moves round to the east at the rate of 1,037 miles per hour, and, as a result, the pressure belts lie (in the southern hemisphere) about 35° S. lat. (high pressure) and 65° S. (low pressure). If, however, the dynamic factor, which largely determines where they shall be, is altered, their positions will alter in accord. If the rotation slightly decreases in velocity, then the belts will be less intense. Thus there will be less warm air driven to the poles, and the temperature will fall greatly." Mr. Taylor does not suggest a possible cause of the retardation. Some wandering body might certainly strike the earth a glancing blow, sufficient to reduce the rotational velocity, and by some means lead up to an ice age, but the earth would require another blow—on the other cheek, as it were—in order to increase the velocity in the reverse direction, after an interval of about 10,500 years, and thus cause an interglacial period. There appears, however, to be some grounds for concluding that the first meeting would be sufficient to relieve us of all further anxiety regarding ice ages.

Quite apart from this impossible hypothetical element, Mr. Taylor has overlooked Fundamental Physical Fact (a) when he states "if the rotation slightly decreases in velocity then the pressure belts will be less intense, and there will be less warm air driven to the poles". As the only air currents which flow from equatorial regions towards the poles are the so-called anti-trade-winds, and these are never below the snow-line for at least 1,800 statute miles, they must therefore lie in a region with a temperature not less than freezing point. In fact, if these currents were warm, they would elevate the snow-line above themselves.

Under these circumstances it is difficult to see how any warmth is conveyed by air currents to polar regions.

No. 20.

M. W. Köppen and A. Wegener account for the quaternary ice age by assuming Wegener's theory of continental displacements to be correct, and explain the succession of glacial and interglacial periods as being due to astronomical causes. The ultimate conclusion arrived at is that the glaciations in the two hemispheres are roughly synchronous, but that a maximum in one hemisphere occurs about 10,000 years before or after a corresponding maximum in the other. Truly this may be described as *roughly* synchronous, or perhaps more correctly referred to as *synchronous but alternate*.

Such conclusions are perplexing, and the argument is difficult to follow.

#### ARE GLACIAL EPOCHS SYNCHRONOUS IN BOTH HEMISPHERES, OR ALTERNATE?

Much time and a great deal of paper and ink have been consumed in debating this question, and as the matter is a very simple one and can be solved in a few minutes, I would like to bring it forward at this stage.

- (a) The earth is spherical in shape.
- (b) The earth revolves on its own axis, and also revolves round the sun.
- (c) The path of the earth is an ellipse.
- (d) The earth's axis is not perpendicular to the plane of its orbit, hence the seasons, spring, summer, autumn and winter.
- (e) When it is summer in one hemisphere, it is winter in the other, and when spring in one, it is autumn in the other.
- (f) The relative movements of the sun and the earth, as well as the other planets in the solar system, and the perturbations due to their mutual attraction have been accurately determined by astronomical observations.

A change in the precession of the equinoxes or in the eccentricity of the earth's orbit would lengthen or shorten our astronomical time-scale; any variation in the amount of sun-heat would affect the trade-winds, the position of the high and low barometric pressure systems, and the

flow of the ocean currents, as regards their position and intensity; any considerable acceleration or retardation of the earth's velocity of rotation would affect atmospheric, and possibly oceanic circulation; large elevations or depressions of land surfaces, especially in the path of the trade-winds, would considerably modify, or possibly completely prevent, glacial conditions attaining severe proportions; but none of these causes, nor any combination of them, could affect the general law that all recurring phenomena on the earth's surface due to earth movement in the solar system are and must continue to be seasonal, so long as the earth retains its spherical form and its axis of rotation remains oblique to the plane of the earth's orbit.

Thus glacial conditions cannot be synchronous in both hemispheres.

Quite apart from these astronomical, geographical and physical reasons, we have the Fundamental Geological Fact (a) (*vide supra*), where the finding of coal seams as far north as lat.  $79^{\circ}$  and as far south as lat.  $85^{\circ}$  is recorded. We also find recorded under Fundamental Fact (b) the discovery of glacial records in lat.  $3^{\circ} 3'$  to  $5^{\circ}$  S. in Africa,  $17^{\circ} 20'$  N. in India, and  $18^{\circ}$  S. in Australia. From these records we must conclude that practically the entire surface of the earth has been at various times covered with snow and ice, and if this had occurred in both hemispheres at the same time, all living warm-climate organisms would have been destroyed. At other times the earth has experienced such heat that vegetation such as that from which coal is formed flourished at the poles, and all cold climate organisms would be eliminated. We know that such has not been the case and thus cannot avoid the conclusion that the glacial epochs were not synchronous but alternate.

In this connection we also have the very definite conclusions arrived at by Charles Darwin,<sup>(28)</sup> who writes as follows: "Should the theory that, whenever the northern hemisphere passes through a cold period, the temperature of the southern hemisphere is actually raised, with the winter much colder, chiefly through the changes in the direction of the ocean currents, while conversely it will be with the northern hemisphere, while the southern passes through a glacial period, be accepted, it throws so much light on geographical distribution of species that I am strongly inclined to trust to it."

In the following twenty-four pages, Darwin shows in the clearest possible manner the influence of ocean currents

in conveying species of animals and plants from island to island, while in other cases the currents set up barriers, which explain the reasons for species being entirely different in regions comparatively close, and with similar climatic and other favourable conditions. The facts given by Darwin are not, of course, proofs of the climatic conditions in both hemispheres being alternate, but rather may it be said that, unless we accept that conclusion, we must assume the distribution of species to be wholly coincidental, or due to separate creations.

#### CROLL'S THEORY.

There now remains only one theory to be discussed, viz. that propounded by Dr. J. J. Croll in the year 1875, in a book entitled "Climate and Time", the fourth and last edition of which was issued in 1890. This last edition contains a list of thirty-seven papers read by Dr. Croll before various scientific societies between 1864 and 1890, relating mainly to glacial epochs and the physical causes thereof. In 1889 he issued "Climate and Cosmology", with the main object of considering the objections which had been raised from time to time against his theory as advanced in "Climate and Time", and also to discuss more fully some comparatively obscure and difficult points in geological climatology.

Notwithstanding Croll's extremely lucid exposition of his subject, I know of no author who has been more misunderstood, misquoted, or misrepresented. This is, no doubt, due to the extraordinary complexity of the subject, involving many physical actions and reactions under constantly changing conditions, and resulting in combinations not by any means easy to express.

On page 12 of "Climate and Time", Croll introduces his theory with the following words: "There is one point to which I wish particularly to direct attention, viz. that I have studiously avoided introducing into the theories propounded anything of a hypothetical nature. There is not, so far as I am aware, from beginning to end of this volume a single hypothetical explanation. The conclusions are, in every case, derived from facts, or from what I believe to be admitted principles. In short, I have aimed to prove that the theory of secular changes of climate follows as a necessary consequence from the admitted principles of physical science."



Within the limits of a paper to be submitted to a scientific society it is, of course, impossible to give more than a very brief outline of a theory involving so many complications and difficulties. Perhaps the best way out of the difficulty is to let Dr. Croll speak for himself (see <sup>(12)</sup>, pp. 14-22, <sup>(13)</sup>, pp. 91-99, <sup>(22)</sup>, pp. 23-29).

As a result of the perusal of Croll's epitome, we know that he accepts the astronomical observations and calculations of Sir William Thomson,<sup>(29)</sup> Leverrier,<sup>(30)</sup> Lagrange, <sup>(31)</sup> p. 273), Sir Geo. Darwin, <sup>(32)</sup> p. 328), Stockwell,<sup>(10)</sup> Sir John Herschel, <sup>(14)</sup> p. 369) and others, regarding the motions and mutual relations of the planets in the solar system, and the inequalities produced by their mutual attractions. He uses Leverrier's famous formula, by which the variations in the eccentricity of the earth's orbit for 3,000,000 years prior to the year 1800 A.D. and for 1,000,000 years after it are calculated.

The variations of eccentricity during the 4,000,000 years are represented diagrammatically in Plate IV, p. 313 of "Climate and Time", and from this we see that the intervals between the times of maximum and minimum eccentricity vary considerably, but in no case is it less than 100,000 years. The conclusion to be drawn from this is that the astronomical conditions are favourable to the occurrence of a glacial epoch on the earth at intervals of about 100,000 years. In other words, the eccentricity of the earth's orbit at intervals of about 100,000 years is such that it is many millions of miles further from the sun when in the aphelion of its orbit than when in perihelion. This would naturally cause a very large difference in the climate of the earth, that hemisphere which had its winter when the earth was in aphelion being covered to a greater or less extent with ice and snow, while the other hemisphere would be enjoying perpetual warmth. Dr. Croll, however, thought it doubtful if this difference, great though it would be, would be large enough to cause a glacial epoch, and this led to the consideration of physical agents, brought into operation by the high eccentricity, which tend to make the cold hemisphere colder and the warm hemisphere warmer as the eccentricity of the earth's orbit increases. With regard to the operation of these agencies it might here be pointed out that A. R. Wallace,<sup>(33)</sup> Dr. J. Geikie,<sup>(34)</sup> Sir Chas. Lyell,<sup>(25)</sup> Sir William Thomson<sup>(29)</sup> and others are in complete accord with Dr. Croll (<sup>(12)</sup>, p. 74, <sup>(13)</sup>, p. 96) and, as no very serious attempt had been made up to the

year 1890 to disprove the general conclusions arrived at by Dr. Croll, and clearly set forth in "Climate and Time" and "Climate and Cosmology", they were generally accepted as correct.

### CRITICISMS OF CROLL'S THEORY.

The criticisms of Dr. Croll's theory which have been advanced since the year 1890 are as follow :

No. 12. E. P. Culverwell, *Geol. Mag.*, 1895, 2, pp. 3-13, 55-65.

Culverwell starts his criticism of Croll's physical theory (referred to as the Astronomical Theory) with a misquotation. On page 4, under the heading of "Statement of Croll's Position", he writes: "In his [Croll's] view the direct effect of the astronomical cause is to lower the terrestrial temperature considerably, and this sets up other agencies, the indirect ones, and these operate chiefly to produce an ice age." Now Dr. Croll's view as given on page 57 of "Climate and Time" is directly opposed to this, and it reads: "When the eccentricity is about at its superior limit, the combined effect of all those causes to which I allude is to *lower* to a very great extent the temperature of the hemisphere whose winters occur in aphelion, and to *raise* to nearly as great an extent the temperature of the opposite hemisphere, where winter of course occurs in perihelion." (The italics are mine.)

This statement of Croll's sets out one of the fundamental conditions of his theory, for it is a *sine quâ non* of his theory that should, from any cause whatever, the temperature of both hemispheres be simultaneously raised or lowered, an ice age could not possibly result. This is so often insisted upon in both "Climate and Time" and "Climate and Cosmology", that it cannot escape the notice of even the most perfunctory reader. Mr. Culverwell, having thus started with a false premise, naturally arrives at inaccurate conclusions.

On page 7 Mr. Culverwell presents a little mathematical puzzle in an illuminating manner. He says: "To show how far even the most extreme midsummer and midwinter temperatures are from being proportional to the sun-heats received at those times, take Yakutsh in Siberia, supposed to be the most extreme of terrestrial climates. The excess of its summer temperature over the  $-239^{\circ}$  F. [the temperature of space] is about  $309^{\circ}$  F., and of its winter temperature about  $199^{\circ}$  F., but the midsummer sun-heat

is to the midwinter sun-heat as 5,800 is to 199, or as 309 is to 11. Hence we may draw two conclusions: if the excess of midwinter temperature over  $-239^{\circ}$  F. be due to the midwinter sun-heat, then, on Croll's theory, the midsummer temperature ought to be  $5800^{\circ}$  F. above the  $-239^{\circ}$  F. [i.e. it ought to be  $5561^{\circ}$  F., or nearly twice the melting point of platinum]; or if on the other hand the summer excess of  $309^{\circ}$  F. be due to the summer sun-heat, then the midwinter temperature ought, if only dependent on sun-heat, to be only  $11^{\circ}$  F. over the  $-239^{\circ}$  F., i.e. it ought to be  $-228^{\circ}$  F.", and so on. Here Mr. Culverwell uses the numbers 5,800 and 11 first as proportional numbers, and then as representing degrees Fahrenheit, and thus obtains results which he himself describes as grotesque. One would think that the very grotesqueness of the results would have called a halt, but Mr. Culverwell continues to make similar calculations on the same page, with similar grotesque results, and on page 9 he sums up with "Thus the foundation of the astronomical theory breaks down completely".

On page 64 he says: "If, either through the earth plunging into a more gaseated region of space, or through some catastrophe, the atmospheric pressure were to be much increased, the resulting increase of temperature might be very great and a genial age might be the result—a rise of  $50^{\circ}$  Fahr. might readily be got"; and he finally concludes with the statement, "No doubt there is much that may fairly be called 'vague speculation' in this suggestion; but there is an advantage even in that, for the more vague it is the more difficult to refute it". It is impossible, I think, to avoid the conclusion that Mr. Culverwell's paper was sent to a scientific society by mistake.

No. 19. Mr. C. E. P. Brooks<sup>(35)</sup> refers to Dr. Croll's theory as "the famous Astronomical Theory of the Quaternary Ice Age". This is not correct, for Croll's theory is not an astronomical theory, nor does it specially refer to the Quaternary or Post-Tertiary age, but deals with glacial epochs of all geological periods, or in other words, it deals with secular changes of the earth's climate.

Mr. Brooks sums up the theory, and dismisses it in one sentence on page 117 thus: "Croll's theory justly points out that the power of a snow surface in reflecting the sun's rays back into space, without their having any warming effect on the earth, is of great importance in the

heat economy of Ice Ages, but apart from this his discussions of meteorological changes, associated with periods of maximum eccentricity, are probably unsound." This is certainly a speedy way of getting rid of an opponent, but it is neither scientific nor convincing. No reasons are given, no statements refuted, no principles debated; the theory is merely stated to be probably unsound, therefore—exit Croll.

No. 22. Dr. G. C. Simpson<sup>(24)</sup> on page 13 of "Past Climates", states: "It is a simple matter of calculation to show that the amount of heat transported in ocean currents is a mere fraction of the amount transported by the air. Thus the chief factor in determining the temperature distribution is the general circulation of the atmosphere . . ."

Now the whole question of the ocean and aerial currents, in relation to the distribution of heat over the globe, has been so exhaustively treated by Dr. J. J. Croll<sup>(12)</sup>, Chaps. 2 and 3, <sup>(13)</sup>, Chap. 2 and p. 82 *et seq.*) that it would be superfluous to write more on the subject. Dr. Croll shows, and his figures have never been questioned, that a greater quantity of heat is conveyed by the Gulf Stream alone from the tropical to the temperate and Arctic regions than by all the aerial currents which flow from the equator, and his statements are borne out by Sir John Herschel, M. Pouillet, Meech, Professor Tyndall, Professor J. D. Forbes and others. Dr. Simpson's use of the phrase "the chief factor in determining the temperature distribution is the general circulation of the atmosphere" really determines the question. (See Fundamental Meteorological Fact (b), *vide supra*.)

It would be interesting to know from Dr. Simpson how his "simple calculation" was made, and thus relieve our minds of much anxiety in regard to this important matter.

Another criticism is that made by Professor A. P. Coleman, whose book "Ice Ages Recent and Ancient" is justly regarded as a standard work for geological students. Some of his physical statements are not, however, in agreement with known facts. On page 275, referring to the question of the glacial epochs being synchronous or alternate in both hemispheres, he says: "There is a close resemblance between the boulder days of North America and of Patagonia; that would hardly be possible if one was many thousands of years older than the other . . . It cannot be doubted that the times of cold were

simultaneous in the two hemispheres and at the equator and no theory that demands alternate glaciation north and south is admissible."

Quite apart from the fact, as shown on page 247, that synchronous glaciation on both hemispheres is a physical impossibility, this sweeping condemnation of a well-thought-out theory is surely very rash and unscientific, based as it is on such very slender evidence. A cursory examination of the records of climatic conditions at present existing between North America and Patagonia would perhaps show Professor Coleman how very slender the evidence is upon which he relies.

### CONCLUSION.

From what has here been written, we must, I think, admit that no salient fact has been brought forward which vitiates the conclusions arrived at by Dr. J. J. Croll forty-five years ago and set out in such a careful, lucid, exhaustive and conclusive manner in "Climate and Time" and the companion volume "Climate and Cosmology".

Our geographical, physical, oceanographical and meteorological knowledge has, of course, advanced since 1890, but all the additional information so gained has tended to confirm the main propositions, or at least to further elucidate the subject.

The principal troubles of most of the critics have resulted from their concentration on details with which they are most familiar, in place of dealing first with fundamental facts. A knowledge of the primary laws relating to any subject will make that subject easier to grapple with, and I know of no study in which this is more evident than the causes which led up to an ice age.

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## CYANOGENETIC GLUCOSIDES IN AUSTRALIAN PLANTS.

PART 5.—*PHYLLANTHUS GASTROEMII*.

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The leaves of *Phyllanthus Gastroemii* collected by one of us (H.F.) in the Eden district in January, 1929, were found to give a positive reaction for hydrocyanic acid with the sodium picrate paper. About a month later a specimen submitted by Dr. H. R. Seddon to the Poison Plants Committee of the C.S.I.R. gave a similar result. These observations threw new light upon the question of the toxicity of this plant, which had long been suspected of poisoning sheep. The uncertainty is reflected in the literature; thus Maiden, in "Plants Reputed Poisonous to Stock in Australia", states that it is supposed to be poisonous in the coast districts, and, similarly, in "Weeds, Poison Plants and Naturalized Aliens in Victoria", Bailey records the fact that, whilst the plant is under suspicion, the evidence is quite unsatisfactory.

*Phyllanthus Gastroemii* J. Muell. is a slender, graceful, euphorbiaceous shrub, growing from two to three feet, and even to twelve feet high, bearing small papery leaves from one-half to three-quarters of an inch long, by half an inch wide. It occurs in all the States, in New South Wales being confined to moist shady situations, particularly in the coastal districts. Under grazing conditions it tends to disappear, being, however, occasionally found cropped by cattle. It has been collected for the present investigation from Eden in the south, Gosford near Sydney, to Coff's Harbour in the north, where it is plentiful in the uncultivated slopes adjoining the banana plantations. We are indebted to the Trustees of National Park for

T—August 5, 1936.



permission to collect a small quantity in that area, and to Mr. G. Scammell for material collected near Glenbrook, in the Blue Mountains. In the Eden district this plant is sometimes known as "purple indigo", on account of the pronounced colour of the stem shown by some, but not all specimens. It is there distinguished from "yellow indigo", by which name *Goodia lotifolia*, another cyanogenetic plant growing in the same district, is known.

To the casual observer, *Phyllanthus Gastroemii* might be confused with *Indigofera australis* and with *Breynia oblongifolia*, both of which it resembles in appearance and habitat; indeed A. Cunningham gave the plant the synonym *Phyllanthus indigoferoides* because of this likeness. Even in the absence of flowers and fruits, however, the alternate arrangement of the leaves distinguishes it from the indigoferas, whilst *Breynia oblongifolia* is characterised by the larger size of the leaves, by their darker colour, and particularly by the fact that on drying they become purplish-black.

The presence of hydrocyanic acid in this euphorbiaceous plant was of particular interest as it had been shown<sup>(1)</sup> in the previous year that *Euphorbia Drummondii*, long suspected of toxicity, was occasionally cyanogenetic; and since it was difficult to obtain the latter in sufficient quantity for a complete investigation, it was thought that an examination of this related plant might throw some light on the toxicity of the group. Specimens of the plant from the National Herbarium, kindly supplied by the then Curator, Mr. Edwin Cheel, were then examined. Although some of these were nearly thirty years old, all gave a positive reaction for hydrocyanic acid, showing that in the dry condition the cyanogenetic substance is stable, unlike that of *Goodia lotifolia*, from which in the dry condition it gradually disappears. The district and the date of collection of the specimens were as follows: Jenolan 1900, Denman 1908, Bellingen 1909, Orara River 1922, Warrumbungle 1901, Toowoomba 1900. Some fifty fresh specimens have been examined, all with a positive result. Specimens of *P. lacunarius* dating from 1896 to 1922 were negative, as was an intermediate form described by Mr. Cheel in 1922; this had been collected by him from Big Jack Mountain. A specimen of *P. thymoides* supplied by Dr. P. Brough was negative, as was one of *P. Ferdinandii*.

QUANTITATIVE DETERMINATION OF HYDROCYANIC  
ACID.

It has become increasingly evident during these investigations that the mere presence of hydrocyanic acid in the products evolved when a plant is subjected to the action of enzymes is only one of a number of factors, each of which may have an important bearing upon its toxicity to animals. Of these factors the *amount* of hydrocyanic acid is important, as is also the presence of a sufficient quantity of suitable enzyme in the plant itself or in the other fodder to which the animal has access. The results in the following table show that the plant contains in the highest yielding samples six times the limit of hydrocyanic acid fixed by Seddon and King<sup>(2)</sup> for a potentially poisonous plant.

AMOUNT OF HYDROCYANIC ACID FROM PHYLLANTHUS  
GASTROEMIL.

| Reference<br>Number. | Date of<br>Collection. | Percentage of HCN<br>Calculated on<br>material dried<br>at 98° C. (with<br>added enzyme). |
|----------------------|------------------------|---|
| 726                  | 4/2/1929               | 0.302   |
| 1599                 | 18/2/1930              | 0.182   |
| 1600                 | 18/2/1930              | 0.170   |
| 1920                 | 15/5/1930              | 0.220   |
| 3295                 | 8/6/1932               | 0.240   |
| 3444                 | 1/6/1936               | 0.108   |

The above results were obtained either on the fresh or on the air-dried plant. The loss in weight in the water oven was determined and the percentage calculated on the material thus dried. The second sample in the above list was dried in the water oven and the hydrocyanic acid then estimated, when 0.138 per cent. was found, pointing to a loss during drying. Specimen 1600 above consisted of the leaves of the pistillate plant. With its own enzyme, specimen 3444 gave only 0.063 per cent., showing a deficiency of enzyme.

EXTRACTION OF THE GLUCOSIDE.  
(With Miss Reichard.)

It has been previously shown that, although alcohol or water is an excellent solvent of cyanogenetic glucosides,

the fact that it is difficult to separate them from the small amounts of accompanying impurities, particularly sugars, etc., makes it preferable to extract the plant with liquids of more limited solvent power. In order to find the most suitable solvent the dried and powdered leaves were successively treated in a Soxhlet apparatus with the solvents mentioned below and the amount of glucoside extracted was roughly ascertained by comparing the colours produced on a picrate paper when portions of the extract, freed from solvent and redissolved in water, were incubated with ground sweet almonds. Petroleum ether after eight hours' extraction had removed no glucoside; ether, ten hours, only a small quantity; ethyl acetate after nine hours proved a better solvent, whilst twelve hours' extraction with acetone removed the whole of the glucoside remaining in the leaves. The solvent action of acetone was then confirmed on another portion of the leaves. The acetone extract from larger quantities of the leaves, made either by boiling with the hot solvent under reflux or by cold percolation, was concentrated to a small bulk, the greenish solid which deposited on cooling was separated by filtration, washed with cold acetone and the acetone solution treated as follows.

#### ISOLATION OF THE GLUCOSIDE.

The acetone solution mixed with one-fifth its volume of benzene deposited after a few minutes some amorphous material similar to that previously filtered off. The filtered liquid was mixed with successive portions of benzene, which now precipitated brown syrups. After three or four such syrupy fractions had been obtained, further additions of benzene gave products which crystallized after a few hours and consisted of the impure glucoside. This was further purified by recrystallization from a mixture of acetone and benzene or from an ethyl acetate solution to which a small proportion of chloroform was added. From the latter mixture or from water the glucoside readily crystallized, especially when approaching purity. In later experiments the acetone extract was refluxed with ethyl acetate, and after concentration chloroform was added. A series of syrups was obtained, from the last of which the impure glucoside crystallized. The yields of pure glucoside were in all cases poor.

The glucoside crystallizes from ethyl acetate and chloroform in flat needles. It has no definite melting

point; when placed in a bath previously heated to  $100^{\circ}$  it gradually decomposed and melted at about  $160^{\circ}$ . If rapidly heated to  $160^{\circ}$ , it melts with decomposition. The dried material underwent a slight change when placed in the bath about  $150^{\circ}$ , and gradually changed up to a temperature of  $167^{\circ}$ , when it decomposed. Impure specimens of the glucoside gave a green colour with ferric chloride, but after recrystallization this property was lost and the pure material gave a faint purple colour with the same reagent. Unlike the benzaldehyde cyanhydrin glucosides, no colour is produced with concentrated sulphuric acid. The glucoside in absolute alcohol is lævo-rotatory,  $[\alpha]_D^{20} -65$ .

On analysis

0.1661 gave 0.3144 of  $\text{CO}_2$  and 0.0906  $\text{H}_2\text{O}=\text{C}$ , 51.6,  $\text{H}=6.1$ .

0.1990 gave 0.3758 of  $\text{CO}_2$  and 0.1070  $\text{H}_2\text{O}=\text{C}$ , 51.5,  $\text{H}=6.0$ .

$\text{C}_{14}\text{H}_{17}\text{O}_7\text{N}\cdot\text{H}_2\text{O}$  requires  $\text{C}=51.1$ ,  $\text{H}=5.8$ .<sup>1</sup>

The glucoside contains water of crystallization which it very slowly loses, after three days in a vacuum desiccator over sulphuric acid, 2.86, and after eleven days, 4.7 per cent.  $\text{C}_{14}\text{H}_{17}\text{O}_7\text{N}\cdot\text{H}_2\text{O}$  requires  $\text{H}_2\text{O}$  5.5 per cent. The dried material gave on analysis, C, 54.2, H, 5.9 per cent.,  $\text{C}_{14}\text{H}_{17}\text{O}_7\text{N}$  requires C, 54.0,  $\text{H}=5.5$ .

#### ACETYLATION OF THE GLUCOSIDE.

The acetylation of the glucoside was conducted by boiling 1.5 grammes with excess of acetic anhydride in the presence of anhydrous sodium acetate in the usual manner. It was first recrystallized from dilute acetic acid, and then from diluted alcohol. It melted at  $142^{\circ}$ . Other specimens had a somewhat lower melting point, but after recrystallization about six times the melting point was raised to  $144^{\circ}$ .

On analysis,

0.129 gave 0.2597  $\text{CO}_2$  and 0.0616  $\text{H}_2\text{O}$ ,  $\text{C}=54.9$ ,  $\text{H}=5.3$ ,  $\text{C}_{14}\text{H}_{13}\text{O}_7\text{N}\cdot 4(\text{CH}_3\text{CO})$  requires  $\text{C}=55.1$ ,  $\text{H}=5.2$  per cent.

#### HYDROLYSIS OF THE GLUCOSIDE.

(With Miss Large.)

The glucoside, 1.168 grammes, was dissolved in 200 mls of water and macerated with 0.1 gramme of emulsin

<sup>1</sup> We are indebted to Mr. C. B. Cox, B.Sc., for these analyses.

at room temperature ( $17^{\circ}$ ) for twenty-one hours. The liquid was then steam-distilled for two hours into a 1% solution of sodium hydroxide. The alkaline solution was acidified and titrated with N/20 iodine solution in the presence of sodium bicarbonate in the usual way. The amount of hydrocyanic acid was 7.2 per cent.;  $C_{14}H_{17}O_7N$  requires 8.2 per cent.

After the removal of the hydrocyanic acid the aqueous liquid in the distillation flask was evaporated on the water bath to a small bulk, filtered to remove a trace of insoluble protein, and when cold extracted with ether. The ethereal solution was dried, the solvent recovered, and 0.33 gramme of a yellow solid was obtained.

#### IDENTIFICATION OF *p*-HYDROXYBENZALDEHYDE.

The yellow solid was soluble in hot water, separating on cooling as an oil which readily crystallized in rhomboidal plates, melting after recrystallization at  $116^{\circ}$  to  $118^{\circ}$  C. The aqueous solution gave a yellow colour with sodium hydroxide and a light purple colour with ferric chloride, indistinguishable from that given by the pure glucoside. With phenyl hydrazine and with *p*-nitro phenyl hydrazine well defined crystalline derivatives were obtained, melting at  $174^{\circ}$  to  $177^{\circ}$  and  $255^{\circ}$  to  $257^{\circ}$  respectively. These were compared by the mixed melting point method with derivatives prepared from *p*-hydroxybenzaldehyde and were found to be identical. A further quantity of this hydrolytic product was obtained by treating the uncrystallizable syrups as described below.

On analysis,

0.0934 gave 0.2356  $CO_2$  and 0.0423  $H_2O$ ,  $C=68.8$ ,  
 $H=5.0$ ,  $C_7H_6O_2$  requires  $C=68.9$ ,  $H=4.9$  per  
cent.

#### THE SUGAR.

After extracting the hydroxyaldehyde from the aqueous liquid with ether as above described, the aqueous liquid was dextrorotatory and gave with phenyl hydrazine and sodium acetate an osazone having the characteristic microscopic appearance of glucosazone. After recrystallization from diluted pyridine it melted at  $198^{\circ}$  to  $199^{\circ}$ , with decomposition.

#### THE IDENTITY OF THE GLUCOSIDE.

It seems possible that the glucoside is identical with dhuririn, isolated from *Sorghum vulgare* by Dunstan and

Henry<sup>(3)</sup> in 1902. Both yield parahydroxybenzaldehyde and glucose on hydrolysis. Unfortunately it is not possible to state definitely that they are identical, as the particulars recorded for dhurrin are incomplete. The melting point was indeterminate, it became brown when heated much beyond 100°, and decomposed at 200°; no acetyl or other derivative was described and the optical rotation was not recorded. Products crystallizing with alcohol and water of crystallization respectively were analysed with satisfactory results. Under these circumstances it is proposed to designate the glucoside now isolated phyllanthin, until such time as it is possible to prepare a specimen of dhurrin for direct comparison and for a more complete study of its properties. Arrangements have been made with Mr. W. L. Hindmarsh, Director of the Veterinary Research Station, Glenfield, for a high yielding form of sorghum to be grown for this purpose.

#### HYDROLYSIS OF SYRUPS. PREPARATION OF *p*-HYDROXY-BENZALDEHYDE.

In order to prepare a further quantity of *p*-hydroxybenzaldehyde for study, some uncrystallizable syrups containing hydrocyanic acid corresponding to about 25 grammes of glucoside were dissolved in a litre of water, to which 100 grammes of ground sweet almonds were added. The whole was incubated at 40° for seventeen hours and at room temperature for another four hours. The liquid had then become de-emulsified and readily filtered, giving a clear solution. It was then extracted with ether ten times, the ethereal solution dried and the solvent recovered, when 16.3 grammes of a brown oily residue were obtained, which became partially crystalline in a few minutes. After some time in the refrigerator the pasty mass was drained on a tile, leaving 2.5 grammes of solid. This solid was contaminated with cyanhydrin, as was shown when 0.28 gramme was steam distilled into dilute alkali. This was titrated for hydrocyanic acid in the usual way and required 16.7 mls of N/20 iodine solution, which corresponds to the presence of 22 per cent. of *p*-hydroxybenzaldehyde cyanhydrin in the material.

The porous pot upon which the hydrolytic product had been drained was broken up and steam-distilled for one hour; hydrocyanic acid corresponding to one gramme of cyanhydrin was indicated by the iodine titration. The aqueous liquid which had been steam distilled was then

evaporated on the water bath, but as it showed signs of oxidation (blackening), the liquid was evaporated under reduced pressure over sulphuric acid in a vacuum desiccator to 100 mils and the *p*-hydroxybenzaldehyde obtained was purified by recrystallization from benzene.

#### ACKNOWLEDGMENTS.

The authors acknowledge with grateful thanks their indebtedness to the Vice-Chancellor of Sydney University for a grant from the Carnegie Research Fund to the Poison Plants Committee of the University of Sydney and the New South Wales Department of Agriculture. Thanks are also due to Professor J. C. Earl, of the Department of Organic Chemistry, for the facilities for the above combustions. We also take this opportunity of thanking Messrs. E. R. Cole, J. T. Tippet and C. D. Musgrave for valuable assistance in this work.

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## EVIDENCE OF A CHANGE OF SEA-LEVEL AT BOTANY BAY.

By C. A. SUSSMILCH, F.G.S.

*(Manuscript received, July 28, 1936. Read, September 2, 1936.)*

In 1896 there was published in the Proceedings of this Society a paper by Messrs. R. Etheridge, Jr., T. W. E. David, B.A., and J. W. Grimshaw, in which they described the occurrence of a submerged forest at Shea's Creek, near Sydney, and pointed out that the occurrence gave evidence for a change of sea-level of at least fifteen feet. Evidence of a similar kind which is considered worthy of being placed on record has now been found at Botany Bay.

Some three years ago three boreholes were put down by the Davis Gelatine Co. at their works at Spring Street, Botany, for the purpose of prospecting for water, the exact location being portions 464 and 465, Parish of Botany, County of Cumberland. My thanks are due to the company for supplying me with the following particulars.

The No. 3 borehole revealed the following section of strata :

|                   |    |               |                                    |
|-------------------|----|---------------|------------------------------------|
| Sand .. ..        | .. | 15 feet       |                                    |
| Peat (1st bed)    | .. | 1 "           |                                    |
| Sand .. ..        | .. | 13 "          |                                    |
| Peat (2nd bed)    | .. | 1 "           |                                    |
| Sand .. ..        | .. | 8½ "          |                                    |
| Peat .. ..        | .. | 0¾ "          |                                    |
| Sand .. ..        | .. | 9 "           |                                    |
| Peat (4th bed)    | .. | 2¼ "          | (horizon of sub-<br>merged forest) |
| Sand with pyrites | .. | 3 to 6 inches |                                    |
| Sand .. ..        | .. | 25 feet       |                                    |
| Layer of pebbles  | .. | 2 to 3 inches |                                    |
| Sand .. ..        | .. | 5 feet        |                                    |
| Peat (5th bed)    | .. | 0½ "          |                                    |
| Sand .. ..        | .. | 13 "          |                                    |
| Peat and mud      | .. | 12 "          |                                    |
| <hr/>             |    |               |                                    |
| Total .. ..       | .. | 106½ "        |                                    |



The depth reached by the borehole was  $106\frac{1}{2}$  feet, and as the mouth of the borehole is 26 feet above sea-level, the lower  $80\frac{1}{2}$  feet of strata are situated below sea-level. It will be noticed that layers of peat occur at six different horizons, and all of these except the topmost one are below sea-level, while the bottom of the borehole was still in a peat deposit, and had not reached bedrock.

Following the completion of the borehole a well some 25 feet in diameter was sunk to a depth of 55 feet, and in this excavation a number of well preserved tree stumps were found associated with the No. 4 peat bed, that is about twenty-nine feet below sea-level; the evidence indicated that these tree stumps were in the position of growth. Immediately below the same peat bed was found a layer of sand three to six inches in thickness, heavily impregnated (to about 53%) with iron pyrites (sulphide of iron).

The beds of peat have undoubtedly resulted from the accumulation of terrestrial vegetation in fresh-water swamps above sea-level; the same process may be seen going on in the same locality today. The occurrence of these peat beds with their associated tree stumps *in situ* now below sea-level therefore indicates an undoubted change in sea-level since they were deposited; either a subsidence of the land or a raising of sea-level. The amount of movement as revealed by the borehole is  $80\frac{1}{2}$  feet, but as the borehole was still in a peat deposit when boring ceased, and as it had not reached bedrock, this  $80\frac{1}{2}$  feet must be looked upon as a minimum, and the total movement may be greater.

Much evidence of a geologically recent change of sea-level, including that of the drowned valleys of Broken Bay, Port Jackson, Botany Bay, etc., has already been recorded, the estimates of the amount of movement ranging up to 240 feet, and it is now generally agreed that this drowning of the shore-line of New South Wales was not due to a subsidence of the land but to a rise of sea-level caused by the immense additions of water to the ocean basins which resulted from the melting of the land ice at the close of the glacial period. The succession of peat beds in the section at Botany would suggest that the rise of sea-level took place in stages, each peat bed representing a period of rest in the upward movement of sea-level.

A STUDY OF PHOSPHATE SOLUBILITY IN  
CERTAIN NEW SOUTH WALES SOILS.

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Communicated by PROFESSOR R. D. WATT.

(With ten text-figures.)

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## INTRODUCTION.

It is well known that the phosphate anion is removed from solution by the soil. As far as the inorganic portion of the soil is concerned, the bases  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$  and  $\text{MgO}$  are considered to be responsible,<sup>(12)</sup> but little is known regarding the structure of the colloidal phosphates which are formed.

Gericke<sup>(7)</sup> and others have shown that the phosphoric acid is present chiefly in the fine particle fractions of the soil. Several investigators (for example <sup>(10)</sup>, <sup>(13)</sup>, <sup>(8)</sup>) have shown that the power of the inorganic colloidal material of the soil to adsorb phosphoric acid varies inversely with the ratio  $\text{SiO}_2 : \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ .

Gaarder concludes from his researches <sup>(5)</sup> <sup>(6)</sup> that the capacity of the soil to bind or to liberate phosphoric acid is determined by the proportions between the bases,  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{MgO}$ , and the acids, silicic acid, "humic acid", carbonic acid, which are dispersed as ions and colloids in the soil.

Britton,<sup>(3)</sup> Teakle,<sup>(15)</sup> Gaarder<sup>(5)</sup> and others have studied the solubility of phosphoric acid at different pH values, when varying proportions of Fe, Al, Ca or Mg are present. With each of these bases there is a characteristic pH range of minimum solubility. Recently Gaarder<sup>(6)</sup> has determined the solubility of the soil phosphoric acid at different pH values. By studying the solubility curve he was able to distinguish the bases with which the phosphoric acid is combined in the soil.

It was proposed to examine the phosphate status of a number of New South Wales soils by determining the

solubility at different pH values of both native and added phosphoric acid. The influence of silicic acid colloid and a "humic acid" preparation on the solubility of the phosphoric acid content of certain acid clays, rich in sesquioxide colloids, was also studied.

#### DESCRIPTION OF SOILS USED.

The soil samples which were used are as follows :

##### Coastal Soils.

1. Pasture soils from the North Coast district; 1A, dark-red clay from Lismore (0-9"); 1B, red clay-loam from Lismore (0-10").

2. Pasture soil from the Central Coast district; light-greyish-brown gravelly loam from Penrith (0-6").

##### Western Soils.

3. North West wheat district; 3A, dark-brown gravelly loam from Curlewis (0-6"); 3B, reddish-brown loam from Narrabri (0-6"); 3C, black clay-loam from Edgeroi (0-9").

4. Central West wheat district; light-reddish-brown loam from Parkes (0-9").

5. South West wheat district; light-reddish-brown loam from Temora (0-7").

Physical and chemical data for these soils are shown in Table I.

#### ANALYTICAL METHODS.

H-ion concentration of soil suspensions was determined electrometrically by the quinhydrone method. A saturated calomel electrode was used as the standard electrode. The procedure recommended by the International Society of Soil Science<sup>(14)</sup> was followed. The results are expressed as pH values.

Phosphoric acid was determined either colorimetrically by the coeruleo-molybdate method of Denigès<sup>(4)</sup> with the modification of Atkins,<sup>(11)</sup> or gravimetrically by the method of Woy.<sup>(16)</sup>

Total phosphorus of soils was determined after fusion with sodium carbonate.<sup>(9)</sup> Exchangeable bases were estimated by the method of Williams,<sup>(18)</sup> after leaching the soil on a filter paper with  $\frac{N}{2}$  acetic acid. The method described by Robinson<sup>(11)</sup> was used for mechanical analysis.

TABLE I.  
*Showing Physical and Chemical Data for the Soils Used.*

NOTE: Percentages are based on weight of air-dried soil.

| Soil No. | Coarse Sand % | Fine Sand % | Silt % | Clay % | Moisture % | CaCO <sub>3</sub> % | Organic Matter (by difference) % | Total Phosphorus % P <sub>2</sub> O <sub>5</sub> | Ratio $\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3}$ of Clay | Exchangeable Bases m.e./100 gm. air-dried soil |       | pH   |
|----------|---------------|-------------|--------|--------|------------|---------------------|----------------------------------|--|--|--|-------|------|
|          |               |             |        |        |            |                     |                                  |  |  | Ca   | Total |      |
| 1A       | 0.3           | 9.8         | 15.4   | 64.6   | 6.77       | 0                   | 3.1                              | 0.241  | 0.75   | 2.8  | 5.7   | 5.0  |
| 1B       | 3.3           | 33.8        | 10.8   | 37.8   | 6.82       | 0                   | 7.5                              | 0.291  | 0.48   | 3.7  | 5.7   | 5.35 |
| 2        | 12.0          | 51.7        | 15.7   | 16.7   | 2.01       | 0                   | 1.9                              | 0.049  | 1.80   | 2.5  | 7.7   | 5.7  |
| 3A       | 28.3          | 30.6        | 10.5   | 21.1   | 3.08       | 0                   | 6.4                              | 0.116  | 2.07   | 12.6   | 14.9  | 8.1  |
| 3B       | 19.3          | 43.7        | 13.8   | 18.6   | 1.62       | 0                   | 3.0                              | 0.060  | 1.64   | 4.1  | 7.0   | 6.95 |
| 3C       | 7.4           | 28.3        | 20.6   | 37.9   | 5.47       | 0.10                | 2.2                              | 0.086  | 1.66   | 15.1   | 23.4  | 8.7  |
| 4        | 43.7          | 28.0        | 8.0    | 18.2   | 1.73       | 0                   | 0.4                              | 0.038  | 1.39   | 5.7  | 7.8   | 7.65 |
| 5        | 1.9           | 55.2        | 17.6   | 22.1   | 2.51       | 0                   | 0.7                              | 0.049  | 1.69   | 5.1  | 8.6   | 6.3  |



TABLE 2.—Continued.

Showing the Solubility of the Soil Phosphoric Acid at Different pH Values.—Continued.

|                |                   |       |       |       |       |       |       |       |       |       |       |       |       |       |       |  |  |  |  |
|----------------|-------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|--|--|--|--|
| Soil<br>No. 3B | c.c. HCl added .. | 15.0  | 5.0   | 2.0   | 1.4   | 0.9   | 0.5   | 0.2   |       |       |       |       |       |       |       |  |  |  |  |
|                | c.c. NaOH added   |       |       |       |       |       |       |       |       |       |       |       |       |       |       |  |  |  |  |
|                | pH ..             | 1.79  | 2.38  | 3.16  | 3.82  | 4.45  | 4.97  | 5.65  | 6.35  | 6.71  | 7.81  | 8.15  | 8.85  |       |       |  |  |  |  |
|                | mgm. $P_2O_5$ ..  | 0.072 | 0.035 | 0.027 | 0.028 | 0.015 | 0.011 | 0.011 | 0.02  | 0.023 | 0.037 | 0.085 | 0.155 |       |       |  |  |  |  |
| No. 3C         | c.c. HCl added .. | 20.0  | 17.0  | 15.0  | 10.0  | 7.0   | 6.0   | 5.0   | 4.0   | 3.0   | 2.5   | 1.5   | 1.0   | 0.5   |       |  |  |  |  |
|                | c.c. NaOH added   |       |       |       |       |       |       |       |       |       |       |       |       |       |       |  |  |  |  |
|                | pH ..             | 2.0   | 2.15  | 2.25  | 2.8   | 3.45  | 3.7   | 4.3   | 4.4   | 4.85  | 5.3   | 6.15  | 7.3   | 7.5   | 8.15  |  |  |  |  |
|                | mgm. $P_2O_5$ ..  | 1.54  | 1.25  | 0.938 | 1.32  | 1.39  | 0.81  | 1.14  | 0.633 | 0.27  | 0.117 | 0.045 | 0.034 | 0.031 | 0.081 |  |  |  |  |
| No. 4          | c.c. HCl added .. | 15.0  | 5.0   | 3.1   | 2.0   | 1.4   | 0.9   | 0.5   | 0.2   |       |       |       |       |       |       |  |  |  |  |
|                | c.c. NaOH added   |       |       |       |       |       |       |       |       |       |       |       |       |       |       |  |  |  |  |
|                | pH ..             | 1.8   | 2.5   | 3.0   | 3.65  | 4.4   | 5.2   | 5.8   | 6.75  | 7.25  | 7.9   | 8.55  |       |       |       |  |  |  |  |
|                | mgm. $P_2O_5$ ..  | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | 0.013 | 0.039 |       |       |  |  |  |  |
| No. 5          | c.c. HCl added .. | 15.0  | 10.0  | 5.0   | 4.0   | 3.0   | 2.0   | 1.0   | 0.5   |       |       |       |       |       |       |  |  |  |  |
|                | c.c. NaOH added   |       |       |       |       |       |       |       |       |       |       |       |       |       |       |  |  |  |  |
|                | pH ..             | 1.89  | 2.05  | 2.54  | 2.73  | 3.00  | 3.48  | 4.28  | 4.95  | 5.99  | 6.79  | 7.79  | 8.28  |       |       |  |  |  |  |
|                | mgm. $P_2O_5$ ..  | 0.028 | 0.027 | 0.013 | 0.011 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | 0.023 | 0.027 | 0.104 |       |  |  |  |  |

## EXPERIMENTAL DATA.

A. The solubility of the soil phosphoric acid at different pH values was determined by the following method:

To 5 gm. of sieved air-dried soil\* (particles  $\leq 2$  mm. diam.) in a 250 cc. stoppered flask was added a solution prepared as follows:

|                              |              |
|------------------------------|--------------|
| x c.c. 0.1899N HCl solution  | } = 100 c.c. |
| y c.c. 0.1468N NaOH solution |              |
| distilled water              |              |

Toluol (1 c.c.) was added to prevent the activity of micro-organisms and the soil suspension was allowed to stand for seven days, shaking for one hour each day in a reciprocating shaking machine. After this period the H-ion concentration of the suspension was determined (15 c.c. suspension was used) and the remainder was filtered with suction through a Jena glass filter of porosity No. 4. The soluble phosphoric acid was determined in a suitable amount of the filtrate and expressed as mgm.  $P_2O_5$  per 100 c.c. filtrate. When a perfectly clear filtrate could not be obtained by this method, a pad of asbestos was prepared on the filter, using B.D.H. asbestos for Gooch crucibles.

The results are shown in Table 2 and illustrated graphically in Figures 1-8.

B. In this case a constant amount of phosphoric acid was added to the soil. The solution was prepared as follows:

|  |              |
|--|--------------|
| x c.c. 0.1899N HCl solution                        | } = 100 c.c. |
| y c.c. 0.1468N NaOH solution                       |              |
| 5 c.c. $NaH_2PO_4$ solution<br>(=1 mgm. $P_2O_5$ ) |              |
| distilled water                                    |              |

The procedure was similar to that used in A.

The results are shown in Table 3 and illustrated graphically in Figures 1-5 and 7 and 8.

C. Silicic acid gel, prepared by precipitating  $Na_2SiO_3$  solution with HCl, was dialysed until free from chloride and suspended in distilled water. Before using, the suspension was dispersed for five minutes in a soil-dispersing machine.

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\* It was not desirable to pulverise or to dry the soil. Special precautions were taken to ensure uniform sampling.

TABLE 3.

Showing the Solubility of the Soil Phosphoric Acid at Different pH Values, after the Addition of  $\text{NaH}_2\text{PO}_4$  Solution  
(=1 mgm.  $\text{P}_2\text{O}_5$ ).

|                |  |                |       |       |       |       |       |       |       |                |                |                   |
|----------------|--|----------------|-------|-------|-------|-------|-------|-------|-------|----------------|----------------|-------------------|
| Soil<br>No. 1A | {<br>pH<br>mgm. $\text{P}_2\text{O}_5$ | 1.62           | 2.26  | 2.93  | 3.71  | 4.58  | 5.14  | 6.02  | 7.02  | 7.95           | 8.66           |                   |
|                |  | $\approx 0.01$ | 0     | 0     | 0     | 0     | 0     | 0     | 0     | $\approx 0.01$ | 0.078          |                   |
| No. 1B         | {<br>pH<br>mgm. $\text{P}_2\text{O}_5$ | 2.07           | 2.25  | 2.73  | 3.19  | 3.57  | 4.29  | 4.76  | 5.72  | 6.39           | 7.17           | 7.94 8.46         |
|                |  | 0.018          | 0.016 | 0.013 | trace | trace | trace | trace | trace | $\approx 0.01$ | $\approx 0.01$ | 0.046 0.092       |
| No. 2          | {<br>pH<br>mgm. $\text{P}_2\text{O}_5$ | 2.03           | 2.54  | 3.20  | 3.98  | 4.76  | 5.12  | 5.69  | 6.28  | 7.24           | 7.94           | 8.38              |
|                |  | 0.255          | 0.18  | 0.126 | 0.108 | 0.379 | 0.403 | 0.526 | 0.521 | 0.526          | 0.695          | 0.792             |
| No. 3A         | {<br>pH<br>mgm. $\text{P}_2\text{O}_5$ | 1.8            | 2.25  | 2.55  | 3.25  | 3.95  | 4.4   | 5.0   | 5.5   | 6.65           | 7.75           | 8.05 8.3 8.4      |
|                |  | 0.295          | 0.25  | 0.309 | 0.175 | 0.15  | 0.353 | 0.368 | 0.50  | 0.517          | 0.577          | 0.658 0.676 0.893 |
| No. 3B         | {<br>pH<br>mgm. $\text{P}_2\text{O}_5$ | 1.76           | 2.38  | 2.82  | 3.91  | 4.65  | 5.26  | 6.23  | 6.80  | 7.32           | 8.43           |                   |
|                |  | 0.758          | 0.61  | 0.463 | 0.455 | 0.463 | 0.49  | 0.556 | 0.61  | 0.61           | 0.833          |                   |
| No. 4          | {<br>pH<br>mgm. $\text{P}_2\text{O}_5$ | 1.8            | 2.5   | 3.0   | 3.65  | 4.3   | 5.15  | 5.6   | 6.75  | 7.0            | 7.5            | 7.8 8.45          |
|                |  | 0.595          | 0.481 | 0.463 | 0.455 | 0.463 | 0.532 | 0.758 | 0.658 | 0.588          | 0.556          | 0.781 0.833       |
| No. 5          | {<br>pH<br>mgm. $\text{P}_2\text{O}_5$ | 1.84           | 2.10  | 2.65  | 3.08  | 3.89  | 4.96  | 5.47  | 5.73  | 6.58           | 7.03           | 7.69 8.26         |
|                |  | 0.411          | 0.245 | 0.17  | 0.123 | 0.135 | 0.174 | 0.248 | 0.492 | 0.455          | 0.625          | 0.658 0.781       |



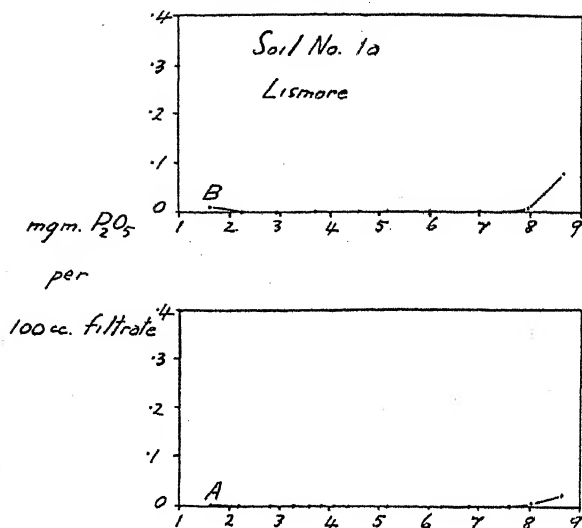


Fig. 1. pH

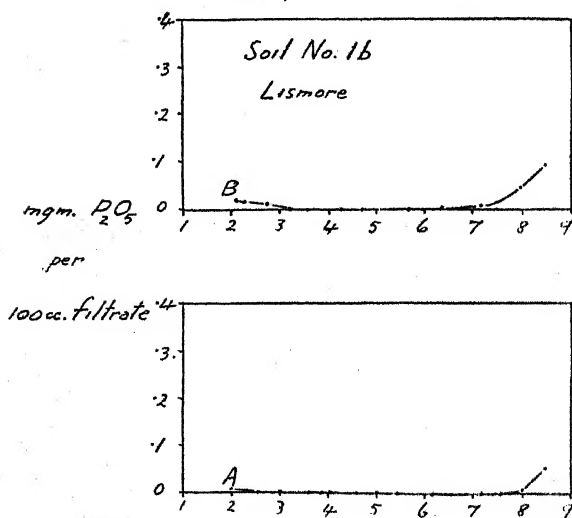


Fig. 2. pH

FIGURES 1-8.

- A. Showing the solubility of the soil phosphoric acid at different pH values.  
B. After the addition of 1 mgm.  $P_2O_5$  as  $NaH_2PO_4$ .

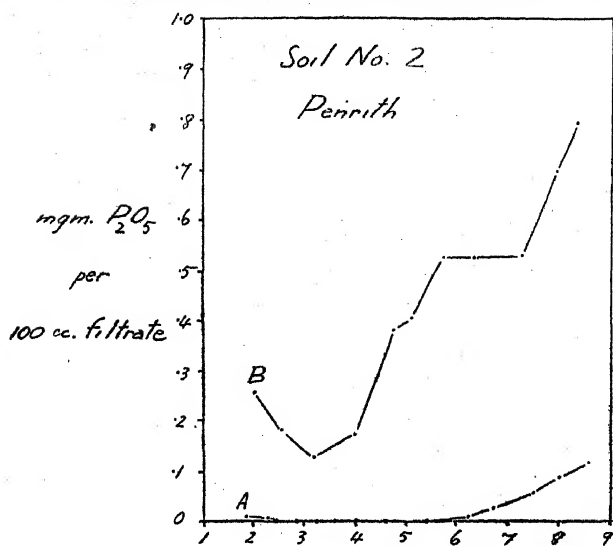


Fig. 3. pH

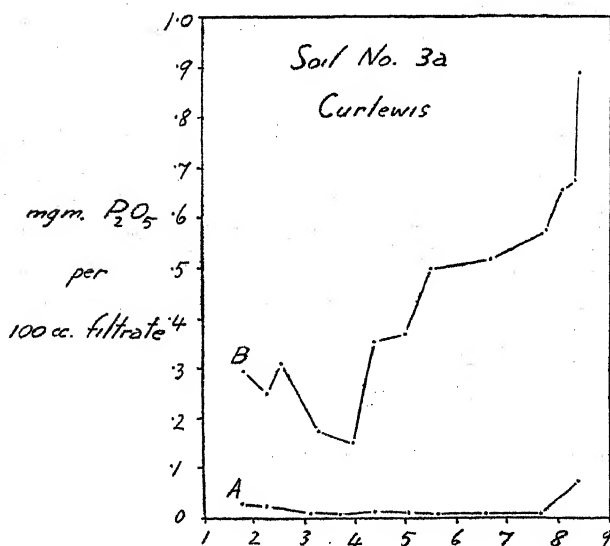


Fig. 4. pH

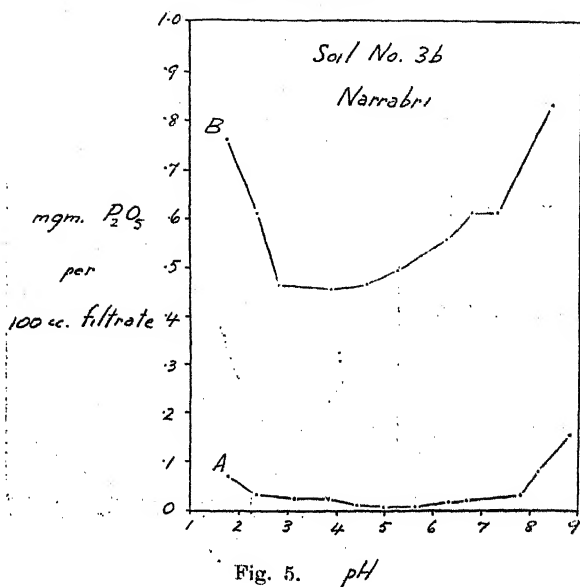


Fig. 5.

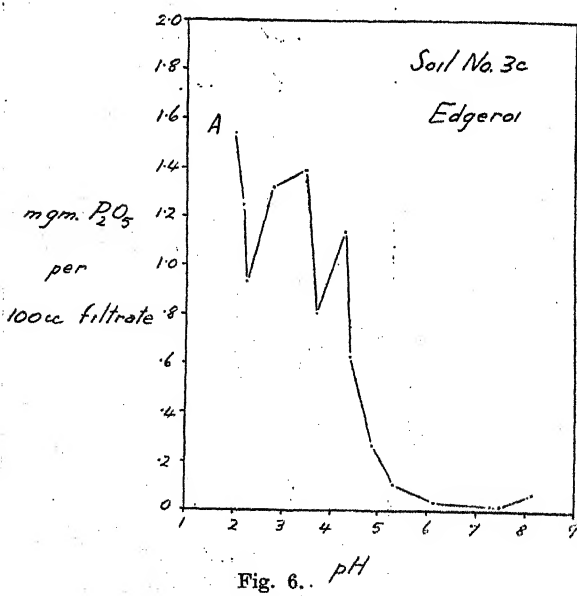


Fig. 6.

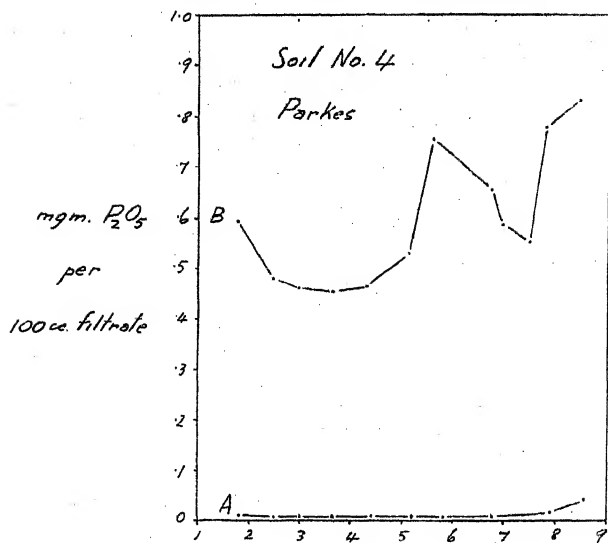


Fig. 7. pH

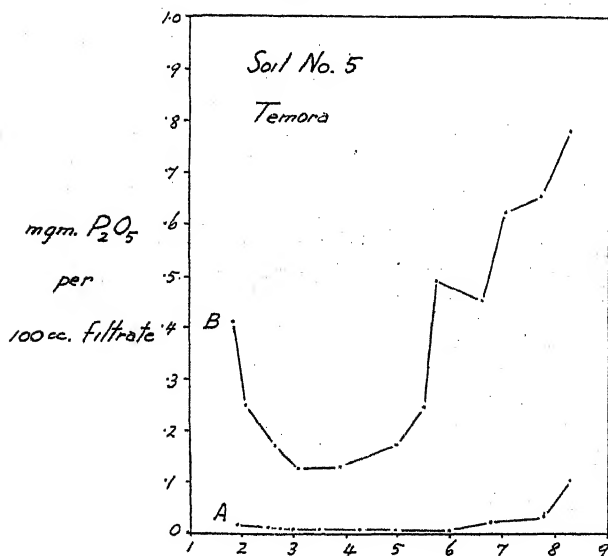


Fig. 8. pH

The effect of silicic acid colloid on the solubility of the soil phosphoric acid was examined in the case of soils 1A and 1B. The solution was prepared as follows :

- |                                 |             |
|---------------------------------|-------------|
| (1) x c.c. 0.1899N HCl solution | } =100 c.c. |
| y c.c. 0.1468N NaOH solution    |             |
| 10 c.c. silicic acid gel        |             |
| (=0.0436 gm. $\text{SiO}_2$ )   |             |
| distilled water                 |             |
| (2) x c.c. 0.1899N HCl solution | } =100 c.c. |
| y c.c. 0.1468N NaOH solution    |             |
| 50 c.c. silicic acid gel        |             |
| (=0.218 gm. $\text{SiO}_2$ )    |             |
| distilled water                 |             |

The procedure was similar to that used in A and B. Silicic acid was removed from the filtrate before making the phosphoric acid determination.

The results are shown in Tables 4 and 5 and illustrated graphically in Figures 9 and 10.

#### DISCUSSION.

In Figure 6 is shown the solubility curve for soil No. 3c, a fertile black clay-loam from Edgeroi. It is seen that above about  $\text{pH}=5.5$  practically no phosphoric acid is soluble, and above about  $\text{pH}=7.8$  only a small amount. An examination of Table 1 shows that this soil has a high  $\text{SiO}_2 : \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$  ratio of the clay fraction, is well supplied with exchangeable Ca, and contains a small excess of  $\text{CaCO}_3$ . Moreover, it has been shown<sup>(3) (5)</sup> that, when an excess of Ca is present, phosphoric acid has minimum solubility in the same pH range, namely above  $\text{pH}=5.5$ . One may therefore conclude that at the normal pH value of this soil ( $\text{pH}=8.7$ ), phosphoric acid is largely combined as basic calcium phosphate (presumably Bassett's "hydroxyapatite"<sup>(2)</sup>). As the pH value falls below  $\text{pH}=5.5$  phosphoric acid is liberated in increasing amounts.

The solubility curve also shows that at  $\text{pH}=3.7$  the phosphoric acid again tends to become insoluble. This pH value coincides with the point of minimum solubility of phosphoric acid when an equivalent amount of Al is present. Below  $\text{pH}=3.7$  phosphoric acid is liberated until at  $\text{pH}=2.3$  there is a third depression in the solubility curve. This is the point of minimum solubility of phosphoric acid when an equivalent amount of Fe is present.

TABLE 4.

*Showing the Solubility of the Soil Phosphoric Acid at Different pH Values, after the Addition of Silicic Acid Colloid  
(=0.0436 gm.  $\text{SiO}_2$ ).*

| Soil No. | pH                                   | 1.99 | 2.29  | 3.01 | 3.51 | 3.95 | 4.50 | 5.04  | 5.74  | 6.49  | 7.14  | 8.05  | 8.58  |
|----------|--------------------------------------|------|-------|------|------|------|------|-------|-------|-------|-------|-------|-------|
| No. 1A   | { mgm. P <sub>2</sub> O <sub>5</sub> | ..   | 0.01  | 0.01 | 0.01 | 0.01 | 0.01 | 0.01  | 0.026 | 0.053 | 0.148 | 0.325 | 0.541 |
| No. 1B   | { mgm. P <sub>2</sub> O <sub>5</sub> | ..   | 0.06  | 2.63 | 3.11 | 3.57 | 4.31 | 5.47  | 6.02  | 6.84  | 7.28  | 7.92  | 8.37  |
| No. 1C   | { mgm. P <sub>2</sub> O <sub>5</sub> | ..   | 0.029 | 0.01 | 0.01 | 0.01 | 0.02 | 0.022 | 0.03  | 0.058 | 0.183 | 0.328 | 0.446 |

TABLE 5.

*Showing the Solubility of the Soil Phosphoric Acid at Different pH Values, after the Addition of Silicic Acid Colloid  
(=0.218 gm.  $\text{SiO}_2$ ).*

[illegible]

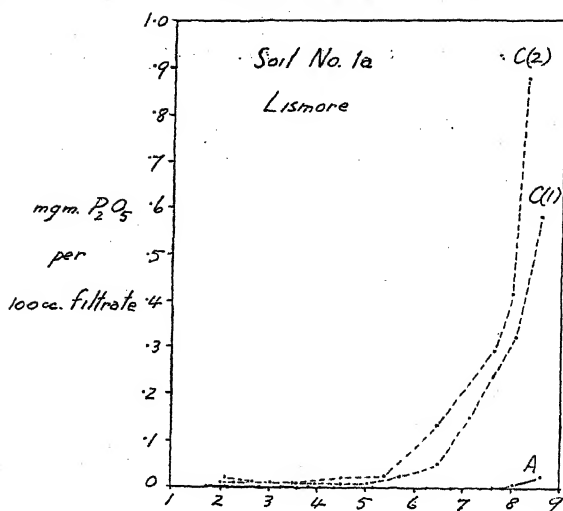


Fig. 9. pH

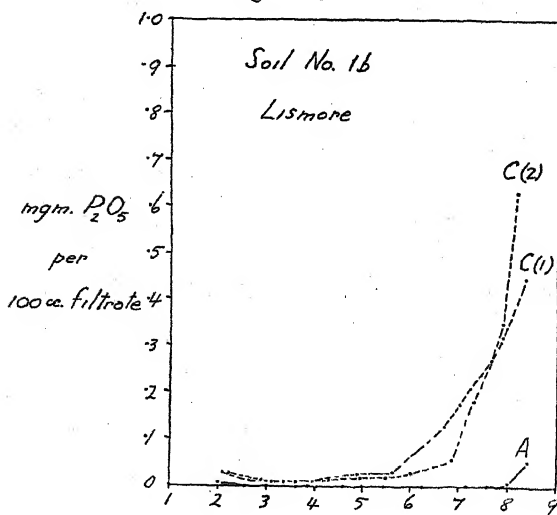


Fig. 10. pH

FIGURES 9 AND 10.

Showing the effect of silicic acid colloid on the solubility of the soil phosphoric acid at different pH values.

A. No silicic acid colloid added.

C (1). Silicic acid colloid added (=0.0436 gm.  $SiO_2$ ).

C (2). Silicic acid colloid added (=0.218 gm.  $SiO_2$ ).

In Figure 7 are shown the solubility curves for soil No. 4, a light-reddish-brown loam from Parkes. It is seen that this soil is extremely poor with respect to soluble phosphoric acid, but the capacity to remove added phosphoric acid from solution is slight. Within the pH range 2.5-5.0, the bases Fe and Al tend to reduce the solubility. From pH 5.5-7.5 there is a depression in the curve due to Ca.

Actually, field experience has shown that this soil type is deficient in available phosphoric acid, since there has invariably been a marked response to superphosphate during the past sixteen years. The solubility curves explain this behaviour, for the solubility of the native phosphoric acid is low and the power of the soil is slight to form combinations which are with difficulty available to plants.

At the normal pH value of this soil (pH=7.65) a solution of  $\text{CaH}_4(\text{PO}_4)_2$  reverts to practically insoluble forms. The reverted phosphate is soluble below pH=6.5, or, when an excess of Ca is present, below pH=5.5. These combinations may therefore be slowly rendered available to plants and micro-organisms by the action of weak acids such as carbonic acid. But in field practice, when superphosphate is drilled in with the seed, it is likely that phosphoric acid is assimilated directly during the early stages of growth. The response shown by small applications of superphosphate is accentuated by the low rainfall conditions prevailing in the western districts. Phosphate manuring stimulates root development and thus the ability of plants to obtain moisture at lower depths.<sup>(17)</sup>

An examination of Figure 8 shows that the phosphate status of soil No. 5 from Temora is similar to that of No. 4. In this soil type, also, superphosphate has invariably shown a marked response.

In soil No. 3A (see Figure 4) the soil phosphoric acid is slightly more soluble than in soils 4 and 5. The added phosphoric acid is not retained strongly by the soil. This soil type has only shown a response to superphosphate in recent years.

In soil No. 3B from Narrabri (see Figure 5), larger amounts of the soil phosphoric acid are soluble within the examined pH range than in soils 3A, 4 and 5. The added phosphoric acid is not bound strongly by the soil. This soil type has not yet shown a response to superphosphate and presumably is not deficient in available phosphoric



acid. But one may expect that when the supply of available phosphoric acid becomes exhausted, other things being equal, this soil will also show a response to superphosphate.

The results obtained with soil No. 2 are illustrated graphically in Figure 3. This soil is extremely poor in soluble phosphoric acid. The added phosphoric acid is removed from solution by the bases Fe and Al within the pH range 3-4. The influence of soil Ca is slight.

In Figure 1 are shown the solubility curves for soil No. 1A, a dark-red clay soil from Lismore. Under the conditions of the experiment, both native and added phosphoric acid are completely insoluble over the pH range 3-8. Above about pH=8 phosphoric acid is liberated. It is to be concluded that in this soil the phosphoric acid is held by a large excess of the sesquioxide colloids, chiefly by hydrated  $\text{Fe}_2\text{O}_3$  <sup>(5)</sup>. Above pH=8 the colloidal basic ferric phosphate becomes hydrolysed and phosphoric acid is liberated. The low  $\text{SiO}_2 : \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$  ratio of the clay fraction (see Table 1) supports this view.

Field experience shows that this soil is markedly deficient in available phosphoric acid, but fails to respond to applications of superphosphate. Liming has no effect. This behaviour is explained by the solubility curves.

The phosphate status of soil No. 1B (see Figure 2) is similar to that of No. 1A.

In Figure 9 is shown the effect of silicic acid colloid on the solubility of the phosphoric acid content of soil No. 1A. Phosphoric acid is liberated in increasing amounts above and below about pH 3-4. Soil No. 1B (see Figure 10) shows similar results. The amount of silicic acid added in C (1) was small in proportion to the soil content of free sesquioxide colloids. The amount added in C (2) was probably not equivalent to the free sesquioxide colloids present. The pH range 3-4 is the range of minimum solubility of phosphoric acid when a moderate excess of Fe is present. It is apparent that part of the soil basoid content is deactivated by the silicic acid colloid (acidoid) and phosphoric acid is liberated.

It must be noted that, since varying proportions of silicic acid appeared in the filtrate at different pH values, the results expressed as mgm.  $\text{P}_2\text{O}_5$  per 100 c.c. filtrate are not exactly comparable. But the volume occupied

by the silicic acid colloid is far too small to alter the interpretation of the results.

Further experimental work was carried out in order to determine whether a natural "humic acid" preparation can also deactivate the sesquioxides in these soils and liberate phosphoric acid. But no means of overcoming the difficulties introduced by the presence of phosphorus in various forms in the preparation have yet been devised. It is hoped to communicate results on this subject at a later date.

#### SUMMARY.

1. Recently, Gaarder has used the solubility of the soil phosphoric acid at different pH values as a means of determining the nature of the combinations of phosphoric acid in the soil.

2. The phosphate status of a number of New South Wales soils was examined by determining the solubility at different pH values within the pH range 1.5-8.5 of both native and added phosphoric acid.

3. In a soil from the "Black Soil Plains" (Edgeroi) it was concluded that the phosphoric acid is combined largely as basic calcium phosphate.

4. In typical red wheat soils from the Central and South West districts, the amount of soluble soil phosphoric acid is extremely small. The soils have little capacity to remove phosphoric acid from solution.

5. In the red wheat soils of the North West wheat district, slightly larger amounts of phosphoric acid are soluble. The soils have little capacity to remove phosphoric acid from solution.

6. In two red clay soils from the North Coast district (Lismore) no phosphoric acid is soluble, under the conditions of the experiment, within the pH range 3-8. Added phosphoric acid is completely removed from solution within the same pH range.

7. It is concluded that in these soils phosphoric acid is held by a large excess of the sesquioxide colloids, chiefly by hydrated  $\text{Fe}_2\text{O}_3$ .

8. It is shown that silicic acid colloid deactivates the sesquioxides in these soils and liberates phosphoric acid.

9. The determination of the effect of natural "humic acid" on the solubility of the phosphoric acid content of these soils is discussed. No entirely satisfactory method has yet been devised.

## ACKNOWLEDGEMENTS.

The author wishes to express his thanks to Mr. G. Wright, University of Sydney, and to Mr. J. N. Whittet, Chief Agrostologist, N.S.W. Dept. of Agriculture, for their interest and advice in connection with this work; also to Mr. H. Govers for assistance in the preparation of Table 1.

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SOME NOTES ON THE PHYSIOGRAPHY OF THE  
LAKE GEORGE REGION, WITH SPECIAL  
REFERENCE TO THE ORIGIN OF  
LAKE GEORGE.

By M. D. GARRETTY, B.Sc.

(With one text-figure.)

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(Manuscript received, September 11, 1936. Read, October 7, 1936.)

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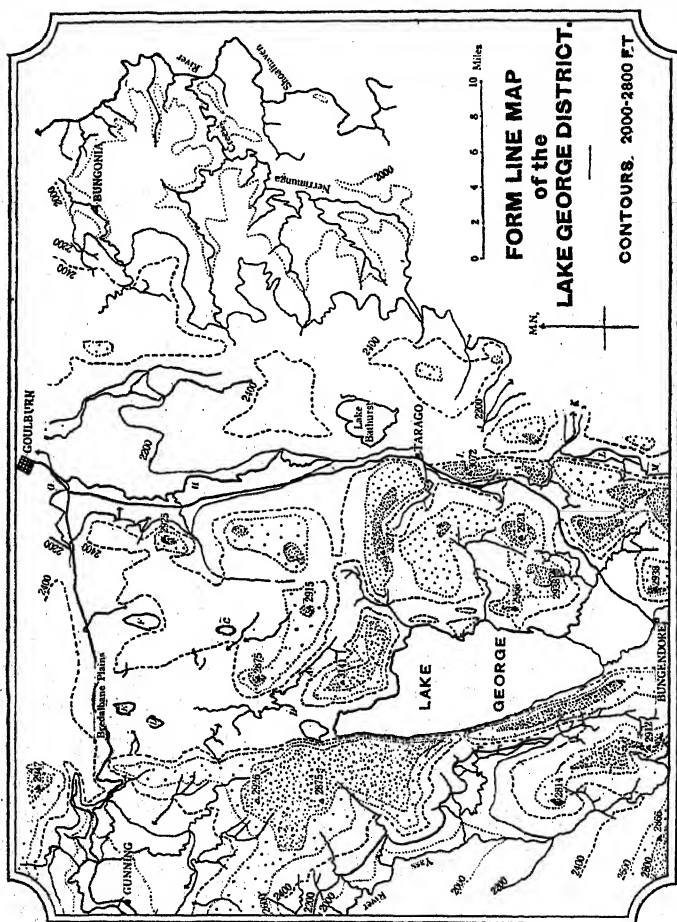
In the course of the geological examination of an area in the vicinity of Lake George, the writer<sup>(1)</sup> was enabled to make some physiographical observations on the Lake George Basin and surrounding country. It is thought that some of the observations may be of interest to other workers in the same field, and, though unfortunately incomplete, they are here presented with that end in view.

The area here considered has been in part the subject of investigation in a series of recent papers by Craft.<sup>(2)</sup> In these he regards the strip between the Shoalhaven River and the Goulburn-Bungendore railway line as belonging to the Shoalhaven Valley, and that between the same railway and the western shore of Lake George is mentioned in his paper on the Wollondilly Basin. A paper concerning the origin of Lake George was published by Taylor<sup>(3)</sup> in 1907.

The accompanying orographical map (text fig. 1) shows the form-lines of the region at intervals of 200 feet. Data used include heights of trigonometrical and railway stations, and aneroid observations by the writer. A paper by Craft has also been drawn upon for part of the area near the Shoalhaven River.

GOULBURN-TARAGO RAILWAY LINE TO SHOALHAVEN  
RIVER.

This section is dealt with very fully by Craft in Parts II, V, and VI of his Shoalhaven series of papers. The tract is part of what he has termed the "Shoalhaven Plain",



Text-figure 1.

Map of the Lake George District, showing form-lines from 2,000 feet to 2,800 feet, and chief elevations. Areas between 2,600 feet and 2,800 feet are lightly stippled. Areas above 2,800 feet heavily stippled. Reference letters: Boro Ck.=J, Collector Ck.=B, Currawang Ck.=A, Dry Lagoon=D, Long Swamp=L, Mulloon Ck.=M, Mulwaree Ck.=H, Reedy Ck.=K, Run of Waters=G, Wet Lagoon=E, Wologorong Lagoon=F, Woolowolar Trig.=I, Tarago Lagoon=C.

cut at an elevation of approximately 2,200 feet (modern), mostly in pre-canyon times.

Mention must be made of the lineament of Mulloon, Upper Boro, and Mulwaree Creeks. These have been considered by Craft (V, pp. 204, 209), and he regards the whole valley as having been formerly occupied by an ancestral Mulloon Creek flowing northwards into the Mulwaree, along the strike of the country. On the entrenchment of the Shoalhaven, Boro and Reedy Creeks cut back and captured sections of it (see text figure 6 in Craft's paper). The writer has noted several facts in accordance with this. High level gravels occur on the eastern shoulders of Woolowolar Ridge, and may also be seen on the opposite side of the valley. The actual "divide" between Reedy and Boro Creeks in this valley was found to be of gravel, implying former stream continuity. Finally, the former presence of basalt in the valley, inferred from the presence of ironstone and laterite, has been proved by the finding of a patch of it still remaining<sup>(1)</sup> and of overlying gravels to the east of Woolowolar trig. station.

Woolowolar Ridge and its prolongations are regarded by the writer as being purely erosional features, and unconnected with any such faulting as was postulated by Craft (1928, p. 637), although he has, by implication, repudiated this hypothesis in a later paper. The ridge is formed of very resistant quartzites and quartz conglomerates for the most part, and is thus in striking contrast with the shale and granite zones to the east and west. At first sight the escarpment from which Sandhills Creek emerges on to the Long Swamp Plain appears to be a fault scarp, but critical examination shows that this is not the case. At this particular point it certainly is impressive, but the effect is not continued to north and south. Probably the excessively canyon-like appearance of the mouth of Sandhills Creek is due to the arrival of the steeply graded Reedy Creek.

The remaining unit of the section under consideration is Mulwaree Creek proper, which flows north to Goulburn, and is part of the Wollondilly system. This stream has eaten its way into the land surface during prolonged stability of grade and base level, and, as seen from the map, has carved out an extensive low-lying area south of Goulburn. From Tarago to Goulburn it has become so

sluggish that it well merits its name of "Mulwaree Ponds". Further mention is made of this feature below.

#### COUNTRY WEST OF LAKE GEORGE PLAINS.

This is quite imperfectly known physiographically as well as geologically. The Lachlan and Yass Rivers and their tributaries, flowing somewhat west of north, have cut into the tableland in such fashion as might be expected in an area possessing alternate belts of hard and soft rocks, striking more or less meridionally. Both rivers show rather steep eastern banks where they run parallel with hard belts, while their western slopes are much more gentle.

#### LAKE GEORGE PLAINS AREA.

For the purposes of the discussion this will be taken as including all the country between the Lake George western escarpment and the Goulburn-Bungendore railway. Only brief mention has been made of it by Craft in his Wollondilly paper, but the block-diagram in that paper is useful (see text figure 7). Although the writer is not in agreement with the mode of origin of Lake George assumed in Craft's paper, the salient topographical facts are given therein, and need not be repeated here. A few points may, however, be mentioned, as being of importance.

The Breadalbane Plains represent the confluence of three drainage systems, and divides between them are difficult to indicate. First there is the Fish River, a headwater of the Lachlan; secondly, there is a gradual slope to the north-east to Run of Waters, draining into the Wollondilly; thirdly, there is a series of marshy pools draining south into Wologorong Lagoon, which has no outlet.

It is of interest to consider the relations of the streams and lagoons of the Lake George Plains. The principal stream is Collector Creek, pursuing a north-to-south course into Murray's Lagoon, just north of the lake. This receives a number of tributaries, such as the much more active Currawang Creek, all of which meet it in boathook bends. This latter fact may be of significance, though it has come to be regarded with some disfavour as a criterion of river capture or reversal of flow (e.g. Browne<sup>(4)</sup>). Collector Creek is sluggish; there is a rise of not more than about 40 feet up this valley from the Lake to the divide between

it and the Breadalbane Plains. This divide itself is marked by the presence of two lagoons, Wet Lagoon and Dry Lagoon. Wologorong Lagoon is mentioned above as having connection to the north with Breadalbane Plains. Tarago Lagoon has an outlet over a low bank of gravel into a tributary flowing north to Collector Creek.

To sum up, the impression given is that the drainage between Lake George and Breadalbane Plains is a meridional one which has lapsed into senility, and is marked by lagoons and marshes.

#### AREA NORTH OF BREADALBANE PLAINS.

North of the Goulburn to Gunning railway line there is an area of distinctly higher country, in which the Upper Wollondilly has incised a valley which has barely reached maturity. A fault has been postulated between this area (not shown on the map) and the Lake George Plains—the Norwood Fault—by Craft (1928) on physiographical grounds. A break here is clearly seen by the traveller along the main southern line who compares the country to his north and south in the vicinity of Breadalbane.

#### THE PROBLEM OF LAKE GEORGE.

The Lake has been explained by Taylor<sup>(3)</sup> as due to the geologically recent formation of a fault throwing to the east along the western margin of the present lake, and the consequent damming of the westerly flowing streams. The evidence he adduces need not be repeated here, but a few points will be noted.

An examination of the map will show (text fig. 1) that consideration of either the general level, or that of the summit plane, on each side of the supposed fault-line does not suggest faulting. Bias may be caused by the large area above 2,800 feet to the north-west of the Lake, but in this area few data are to hand; the area shown on the map is certainly a maximum, and should perhaps be really much smaller. Again, the actual peaks indicate a much greater height (up to 3,327 feet) to the east of the line than to the west. This effect of continuity of surface would have been even better portrayed by an extension of the map further southwards.

The map also shows that characteristic valley systems occur in uninterrupted fashion in the Yass and Lachlan basins on the west, and the Wollondilly basin on the east



(Mulwaree Creek). The Lake George western escarpment and its less imposing meridional extensions appear to play the rôle of a normal headwater ridge between two river systems. The contrasts drawn by Taylor between the degree of development and grade of streams on the eastern and western sides of the escarpment were found on examination by the writer to be of doubtful strength.

With regard to the so-called antecedent Molonglo and Fish Rivers, the latter near Cullerin has been described by Craft (1928) as entrenched by the uprising of the Cullerin scarp, but it seems to the writer to be no more youthful in appearance here than are parts of such normal streams as Sandhills Creek (headwaters of Reedy Creek), and to demand no special explanation. The case of the Molonglo seems to have been rather exaggerated by Taylor. Certainly it has a fairly wide headwater valley, and a rather restricted middle valley, but so also have other streams which cut through resistant ridges but expand in softer rocks upstream. A topical example is Merigan Creek (headwaters of Mulwaree Creek), with flood-plains half a mile wide, but lower down narrowing greatly in the vicinity of the more resistant ridge near Tarago. Contortions in the sections of the so-called scarp in the Molonglo district were thought by Taylor to constitute evidence of crushing near the fault. Such contortions have also been noted by the writer about two miles west of Bungendore, but he thinks that they must all be much older than Tertiary. In fact the formation of such folding, in preference to brecciation, so near the surface in late Tertiary time seems quite unlikely.

The importance of the high-level gravels south-west of Geary's Gap is difficult to assess. The facts as given by Taylor seem undoubtedly to point to a former north-westerly flow of a stream, of fairly steep grade, across their position on the present escarpment. An examination in the field confirms this view. The question arises, however, as to the antiquity of such a stream (the idea of lacustrine origin seems untenable for various reasons, including slope of the base of the formation). Little importance can be attached to the unconsolidated nature of the gravels from the point of view of age, since gravels may persist in this way to an amazing extent. A case in point is that of the pre-canyon gravels and clays of the Shoalhaven Valley; thicknesses of these up to 80 or 100 feet have been seen sawn through by the gorges of such

streams as Nerrimunga Creek. On the latter, near Jasper's Gully, such a truncated deposit stands literally on the edge of a gorge 1,200 feet deep, and seems stable. Again, as shown in the very section given by Taylor, dissection of the postulated stream channel in a crosswise direction has been considerable—and that accomplished by mature streams. It thus seems quite feasible that the gravels could be relics of a long extinct cycle of erosion in which the local base-level was at (about) the relative height of the present ridges. An objection to this view may be based on the presence, on the lake floor, in the same line as the gravels, of what is apparently a silicified gravel or "grey billy". This differs, however, in the important respect of silicification, and could easily be due, in its present position, to an outpouring of basalt, now removed, on to the low-lying area of the lake floor. This explanation would indeed tend to suggest the pre-Pliocene existence of the present low-lying lake area.

It should be mentioned that the suggestion by Taylor of the lake silt's being about 200 feet thick is merely an expression of opinion. The writer is not aware of any evidence for a depth greater than thirty feet—that reached by wells sunk into the lake. The contouring of the bedrock of the lake would perhaps form a fit subject for investigation along geophysical lines.

#### TENTATIVE SUGGESTION AS TO THE ORIGIN OF LAKE GEORGE.

Although sufficient work has not been done to justify a definite conclusion on the matter, one is emboldened to suggest an alternative mode of origin for Lake George and its associated escarpment.

The features of drainage mentioned above make it clear that a small northward tilt of the Lake George Plains area would convert it into a normal stream system passing into either the Fish or the Wollondilly system. The suggestion is made that down-warping of the area relative to the country to the north took place along the Norwood Fault—or Warp. Instead, however, of a clean break at this point, a kind of ramp was formed, by a general tilt to the south, or by a series of small warps. Precedent for this is found in the block to the north of the Norwood Fault in that there is a gradual rise or tilt upwards from Tarlo to Taralga. There seems no reason why this should not also have been the case to the south. Such tilting would cause stagnation

of the Lake George River system, and cause the formation of the lake itself as well as the numerous lagoons. It may also have played its part in the stagnation of Mulwaree Ponds. Local irregularities in the tilting, perhaps a sagging, or local faulting, would be competent to cause the formation of transient base-levels, or pene-base-levels, along the stream and its tributaries, at which would be deposited alluvial fans and gravel beds. Failing these tectonic irregularities, even antecedent irregularities in the stream gradient, due to such causes as differential hardness, would be empowered by a regional lowering of the gradient to cause such deposits. Perhaps to these causes the gravel barriers of Tarago Lagoon and others, and even that between Lake George and Murray's Lagoon, are due. This latter conspicuous gravel bank is by its very size grossly out of keeping with the storm hypothesis of Taylor.

On this view the western escarpment of Lake George must depend for explanation on differential erosion. Although the argument in this paper has been directed at discounting the presence of a fault scarp of late Tertiary or post-Tertiary age, it does not exclude the existence of older faulting, of Silurian age, for example, but the evidence for such an uncovered fracture, or fault-line scarp, is entirely wanting at present. In any case the present explanation of differential erosion would not be thereby affected. Escarpments just as impressive and due to differential erosion are to be found at Michelago and other places between Cooma and the Federal Capital Territory. Examination of the geology of the Lake George escarpment reveals evidence in favour of an erosional origin. It is composed in large part of relatively hard felsite and porphyry bands, outcrops of shales, as at Geary's Gap, resulting in a notable lowering of the ridge. Numerous instances of meridional ridges in the region shown on the map have been verified as consisting of resistant rock-types. The fact that the strike of the rocks is parallel to the old Lake George River system would considerably aid the formation of the ridge. Of great significance also is the fact that in the actual escarpment the dip of the rocks is to the west, resulting in accentuation of the slope on the east, and its modification on the west. The fact that the escarpment supports rock *débris* and alluvium, with stable vegetation on them, points to its own stability, and discounts the statement that it is being "actively eroded".

## SUMMARY.

The region considered is comprised of several distinct sections : (i) The Shoalhaven Plain, from Tarago to the Shoalhaven ; (ii) the headwater districts of Lachlan and Yass Rivers ; (iii) Lake George Plains, with lagoons and senile drainage ; (iv) the Norwood Warp. The significant features of each are discussed where pertinent to the origin of Lake George. The evidence for Taylor's fault hypothesis is examined from a number of aspects, and the tectonic origin of the western escarpment questioned. An alternative explanation based on stream development and gentle warping is tentatively submitted.

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## THE ACTION OF LEAD TETRACHLORIDE ON PRIMARY AND SECONDARY HALOGENATED ARSINES AND ON TERTIARY ARSINES.

By G. J. BURROWS, B.Sc.,  
and A. LENCH, B.Sc.

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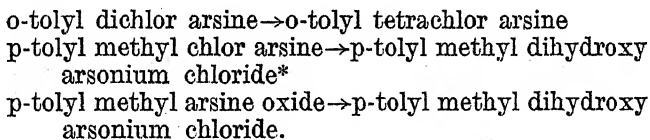
The experiments recorded in this paper were carried out after an unsuccessful attempt to prepare coordination compounds of tertiary arsines with plumbous halides. In view of the fact that stannic iodide gives an addition compound with phenyl dimethyl arsine (Burrows and Turner, *J.C.S.*, 1920, 117, 1373), it was thought that it might be possible to obtain an analogous derivative with a tertiary arsine and lead tetrachloride, in spite of the fact that the latter is a strong oxidising and chlorinating agent (Seyewetz and Tatu, *Bull. Soc. Chem.*, (IV) 1926, 39, 647). The authors realised that this reagent would very probably oxidise a tertiary arsine to an arsine dichloride, but it was hoped that by keeping the temperature very low it might be possible to isolate a compound of the arsine with the lead tetrachloride, or, as an alternative, a compound of lead tetrachloride with the oxidation product of the arsine.

Unfortunately no addition compound of any type was isolated, although we obtained fairly definite evidence of the formation of a very unstable compound of lead tetrachloride and a tertiary arsine. At the same time we have been able to compare the action of lead tetrachloride with that of chlorine on arsines.

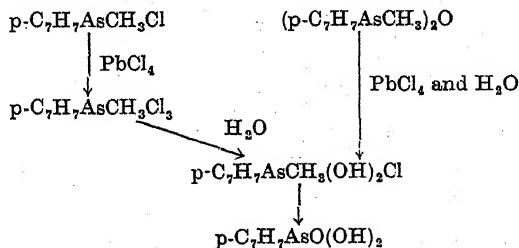
When a dilute solution of the arsine (either phenyl dimethyl arsine, diphenyl methyl arsine, or phenyl methyl ethyl arsine) at  $-5^{\circ}\text{C}$ . was slowly added to a dilute chloroform solution of lead tetrachloride at the same temperature, a reddish brown solid immediately separated. This could not be isolated, as it very quickly decomposed to white plumbous chloride. At room temperature the reaction was violent. In all cases the lead tetrachloride was reduced to plumbous chloride and the arsine oxidised.

The oxidation product varied with the arsine; in the case of diphenyl methyl arsine, or phenyl methyl ethyl arsine, the dichloride was isolated, whilst from phenyl dimethyl arsine the dichloride could not be obtained. On allowing the concentrated solution to stand (exposed to air), phenyl dimethyl arsonium hydroxy chloride separated, evidently resulting from the hydrolysis of the dichlor- or tetrachlor arsine by the moisture in the air. The chlor addition compounds of the different tertiary arsines appear to vary considerably as regards their ease of hydrolysis and their affinity for water.

In view of the energy of the above reaction it was decided to study the action of lead tetrachloride at low temperature on halogenated primary and secondary arsines and to compare it with chlorine as a reagent for the addition of chlorine to arsines. It was found to be an ideal reagent for this purpose, and the reaction could be kept well under control, the oxidised products being obtained in good yield. The various types of oxidation are represented by the following :



In the case of the two latter reactions it was noticed that, if the temperature was allowed to rise above  $10^{\circ}\text{C}.$ , a secondary reaction took place, with the elimination of the methyl group and conversion of the arsonium derivative to p-tolyl arsonic acid :



\* The hydroxy chloride separated on allowing a concentrated solution to stand exposed to the air. Apparently the chlor addition compound (if formed) absorbed moisture from the air and then hydrolysed.

It was subsequently found that p-tolyl methyl arsenic acid was converted by lead tetrachloride to p-tolyl arsonic acid in a similar manner. This reaction, involving the elimination of a methyl group attached to the arsenic atom, recalls the slow oxidation of tertiary arsines by atmospheric oxygen in the presence of moisture to arsonic acids. (THIS JOURNAL, 1934, 68, 72).

#### EXPERIMENTAL.

*Phenyl dimethyl hydroxy arsonium chloride*,  $\text{PhMe}_2\text{As}(\text{OH})\text{Cl}$ , was first prepared by Steinkopf and Schwer (*Ber.*, 1921, 54, 2791) by the action of hydrochloric acid on phenyl dimethyl arsine dihydroxide in alcohol. It was later prepared in quantity by the oxidation of phenyl dimethyl arsine with perhydrol in the presence of hydrochloric acid (Burrows, THIS JOURNAL, 1935, 68, 76). In the present work it was obtained by the action of lead tetrachloride on phenyl dimethyl arsine in chloroform solution at  $-5^\circ \text{C}$ . After the initial vigorous reaction was completed, the plumbous chloride was removed and the filtrate concentrated. The crystalline mass which separated after standing for some time was washed with benzene, recrystallised from chloroform and then from alcohol in fine colourless needles. It had the properties previously assigned to it, and was identified by its melting point and equivalent weight.

*Diphenyl methyl arsine dichloride*,  $\text{Ph}_2\text{MeAsCl}_2$ , was prepared (1) by the action of chlorine on diphenyl methyl arsine in chloroform solution, and (2) by the action of lead tetrachloride on the arsine. For the latter preparation a dilute solution of lead tetrachloride (1 mol. +5% excess) in chloroform was added to a chloroform solution of diphenyl methyl arsine at  $-5^\circ \text{C}$ . The solution quickly became hot and plumbous chloride separated. After removal of the latter, the filtrate was concentrated, and on cooling a yellow crystalline precipitate separated. This was recrystallised twice from chloroform. The compound was obtained in the form of lustrous highly refractive prisms melting at  $132^\circ \text{C}$ . It has a slight odour, is slightly soluble in cold benzene, and readily soluble in the same solvent on heating. It is insoluble in carbon tetrachloride, soluble in acetone, and very soluble in water, giving an acid reaction to litmus, due to hydrolysis to the hydroxy chloride and hydrochloric acid. It is not hygroscopic.

Found: Cl=22.2, As=23.6 per cent. M. wt. in benzene, 316, 318, 317.

$C_{13}H_{13}AsCl_2$  requires Cl=22.5, As=23.8 per cent. M. wt., 315.

*Phenyl methyl ethyl arsine dichloride*,  $PhMeEtAsCl_2$ , was prepared from phenyl methyl ethyl arsine by the action of (1) chlorine in chloroform, or (2) lead tetrachloride in chloroform at  $-5^\circ C.$ , as in the preparation of the previous compounds. The product in this case was recrystallised from acetone, then chloroform, and finally from carbon tetrachloride. It was obtained in the form of colourless needles melting at  $83^\circ C.$  It was found to be very soluble in chloroform, acetone and benzene, less so in carbon tetrachloride, and insoluble in ether. The compound is hygroscopic, and is soluble in water giving an acid reaction to litmus.

Found: Cl=26.6, As=27.6 per cent. M. wt. in benzene, 264, 273.

$C_9H_{13}AsCl_2$  requires Cl=26.6, As=28.1 per cent. M. wt., 267.

*o-Tolyl arsenic chloride*,  $C_7H_7AsCl_2$ , was prepared by La Coste and Michaelis (*Ann.*, 1880, 201, 184) by the action of chlorine on o-tolyl dichlor arsine. In the present work it was obtained by adding a dilute chloroform solution of lead tetrachloride at  $-5^\circ C.$  to a chloroform solution of o-tolyl dichlor arsine at the same temperature. The reddish yellow solid first formed quickly decomposed with the formation of plumbous chloride. The pale brown solution finally became yellow. After removal of the plumbous chloride, the chloroform was distilled under diminished pressure, leaving a yellow viscous liquid which was stable in dry air. It could not be distilled.

Found: Cl=45.6 per cent.

$C_7H_7Cl_2As$  requires Cl=46.1 per cent.

On treating p-tolyl dichlor arsine with lead tetrachloride in chloroform as above, it was not possible to isolate the corresponding p-tolyl arsenic chloride. Reaction occurred as before with the separation of plumbous chloride, but on concentrating the filtrate by distilling the chloroform, p-tolyl dichlor arsine was recovered. (It was identified by its melting point and also by analysis.) This result would seem to indicate that, unlike the ortho compound, p-tolyl arsenic chloride is unstable and breaks down to the dichlor arsine with liberation of chlorine.



*p*-Tolyl methyl dihydroxy arsonium chloride,  $p\text{-C}_7\text{H}_7\text{MeAs}(\text{OH})_2\text{Cl}$ . The preparation of this compound from *p*-tolyl methyl arsinic acid and also from *p*-tolyl methyl arsine oxide has already been described by one of us (THIS JOURNAL, 1935, 68, 78). In the present investigation it was obtained by adding a chloroform solution of lead tetrachloride at  $-5^\circ\text{C}$ . to one of *p*-tolyl methyl chlor arsine, with vigorous stirring. The reaction was found to be violent, a reddish brown compound at first separating. After a few seconds this decomposed to plumbous chloride and the solution became yellow, and finally red. The latter colour change was a definite indication of the completion of the reaction. After removing the plumbous chloride the filtrate was concentrated, and, as it did not crystallise on cooling, the solution was allowed to stand. After a couple of days the crystalline product which had separated was removed and recrystallised from chloroform in large plates, and then from acetone in microcrystalline lustrous leaflets melting at  $133^\circ\text{C}$ . It was found to be identical with the compound previously described (*loc. cit.*).

Found: Cl=14.3 per cent. E. wt.=124.5.

$p\text{-C}_7\text{H}_7\text{CH}_3\text{As}(\text{OH})_2\text{Cl}$  requires Cl=14.2 per cent. E. wt.=125.3.

On adding this compound to an excess of water a white oil was precipitated and this quickly solidified. On recrystallisation from alcohol, colourless needles were obtained, which melted at  $151^\circ\text{C}$ ., had an E. wt. of 214, and were identified as *p*-tolyl methyl arsinic acid. *p*-Tolyl arsonic acid was obtained along with the above compound by the action of lead tetrachloride on *p*-tolyl methyl chlor arsine or *p*-tolyl methyl arsine oxide in chloroform solutions if the temperature was allowed to exceed  $10^\circ\text{C}$ . Being less soluble in chloroform than the hydroxy chloride, it separated from solution first, and was purified by taking advantage of its insolubility in carbon tetrachloride, in which liquid the hydroxy chloride is readily soluble. The average yield when the preparation was carried out at room temperature was about 8 per cent. If the solutions were warmed before mixing them, the arsonic acid was the main product.

It was subsequently found that *p*-tolyl methyl dihydroxy arsonium chloride in boiling chloroform yielded an appreciable amount of *p*-tolyl arsonic acid on treatment with lead tetrachloride. A similar result was observed when a solution of *p*-tolyl methyl arsinic acid in hot acetone

was treated with this reagent. It would appear therefore that lead tetrachloride (in chloroform solution) is a useful reagent in removing a methyl group attached to arsenic, probably as methyl chloride, at the same time maintaining the oxidised state of the molecule. In all cases the p-tolyl arsonic acid was identified by its equivalent weight (108) and a mixed melting point determination with a known sample of the acid. p-Tolyl arsonic acid melts with decomposition at about 355° C.

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[NOTE.]

DIPHENYL DIHYDROXY ARSONIUM CHLORIDE,  
 $\text{Ph}_2\text{As}(\text{OH})_2\text{Cl}$ .By G. J. BURROWS, B.Sc.,  
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*(Manuscript received, September 15, 1936. Read, October 7, 1936.)*

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La Coste and Michaelis (*Ann.*, 1880, 201, 230) obtained a white powder which they described as diphenyl arsenic oxychloride;  $\frac{\text{Ph}_2\text{AsCl}_2}{\text{Ph}_2\text{AsCl}_2} > 0$ . Although the compound was soluble in hot benzene, they were unable to crystallise it, and they recorded the melting point of the powder as  $117^\circ\text{C}$ . In arriving at the above formula, the authors appear to have been largely influenced by their yield; they apparently did not determine directly the percentage of chlorine in the compound.

The formation of such an oxychloride is most surprising; in fact this is the only oxychloride of this type recorded in the literature. One would expect diphenyl arsenious oxide to behave in the same way towards chlorine as other secondary arsenious oxides, in which case the compound described by La Coste and Michaelis would be diphenyl dihydroxy arsonium chloride. To establish the correctness of this view it was decided to repeat the preparation of the compound.

In their paper La Coste and Michaelis failed to state what liquid they used as solvent for the diphenyl arsenious oxide. In the present investigation chloroform was used for this purpose.

When dry chlorine was passed into a cold chloroform solution of the oxide the latter became hot, and the product gradually separated in the form of short white prisms. After recrystallising twice from chloroform, the compound was found to melt at  $128^\circ\text{C}$ . The compound had a slight sweet odour, was stable in air, insoluble in cold, but somewhat soluble in hot benzene, insoluble in cold water,

but dissolving to a certain extent on heating, giving an acid reaction to litmus as a result of hydrolysis to diphenyl arsenic acid and hydrochloric acid.

Found: Cl=11.9 per cent., E. wt. [determined by titration with  $\text{Ba}(\text{OH})_2$ ]=149.6.

$(\text{C}_6\text{H}_5)_2\text{As}(\text{OH})_2\text{Cl}$  requires Cl=11.9 per cent. M. wt.=298.5. (E. wt.=149.3.)

The formula of La Coste and Michaelis requires Cl=23.1 per cent.

These results indicate that the compound is diphenyl dihydroxy arsonium chloride.

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## INTERFERENCE BY REFLEXION FROM A CONCAVE SPHERICAL MIRROR.

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(With Plate VII and four text-figures.)

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### 1. INTRODUCTION.

Sharp and striking interference bands can be obtained by the following simple arrangement, which I have not seen described elsewhere. A spherical concave mirror is placed on a spectrometer table with its centre of curvature in or near the plane of the axes of collimator and telescope; a parallel beam of monochromatic light from the collimator falls on the mirror at a large angle of incidence (varying of course from point to point on the surface); on examining the reflected light through the telescope one or more superposed systems of bands are to be seen, the character varying with the dimensions of the mirror and with the angles between the axes of collimator, telescope, and mirror. With a given mirror positions favourable for the observation of the bands are readily calculated by methods indicated in the discussion given later.\*

These bands are the result of interference between beams which have been reflected at the concave surface different numbers of times; generally one beam has been reflected once, and others two, three, or more times. By the use of screens appropriately situated as described below bands corresponding to beams reflected respectively twice and three times, and to other pairs can be obtained.

Similar bands can be observed with divergent or convergent light, and the lens of collimator or telescope, or both, may be removed, the intensities and positions of the bands being altered thereby. If parallel incident

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\* Mr. W. F. Gale, F.R.A.S., informs me that he has observed these bands, but has never read any explanation or discussion concerning them.

light is employed, the telescope may be removed, the bands being viewed through an eye-piece which may be moved from place to place. With this arrangement, if the eye-piece is focussed on to a point on the radius of the sphere parallel to the incident beam, that is on the second focal line of the mirror, the bands seen there are sharply defined at the ends and are of practically uniform intensity throughout their height, which here is proportional to the length of the slit with which we shall assume the collimator provided. The photographs in Plate VII have been taken without any focussing lens beyond the collimator; the plate was near the second focal line but not parallel to it.

The origin of these bands is readily seen from the diagram in Fig. 1, where the matter is discussed as one in two dimensions. A ray incident at C is deviated by the single reflexion through an angle  $\theta$ , while a parallel incident ray is deviated through  $\theta/2$  at A and at B. The two combine in the telescope to give an effect depending on the relative amplitudes and on the phase difference, which is proportional to the differences between the paths, AB and  $2CM$ , if phase change at reflexion may be neglected. A second ray incident at C' is deviated through a different angle  $\theta'$  and this interferes with one undergoing reflexion through  $\theta'/2$  at A' and B'; in this case the path difference is not the same as in the former, and as a result interference bands are seen. For small values of  $\theta$  the path difference is proportional to  $\theta^3$  and the distance between bands therefore inversely proportional to  $\theta^2$ . (See Section 4.)

In Fig. 2 it is seen how more complicated interference patterns are obtained. Here we have beams reflected once, twice and thrice, giving two systems of bands as shown in the position *p*, *q* of photograph A, and in E, Plate VII. The possibility of interfering beams with greater numbers of reflexions is obvious, the conditions for these being readily determined for a given mirror. In the portion *qq'* of A in the Plate, we see a complex pattern due to several beams interfering. In such a case, by interposing a screen S, one or more of the interfering beams may be cut out, with consequent simplification of the pattern. In B, C and D in the Plate we see effects obtained by placing S in various positions; at each end of B we have bands due to beams 2 and 3 (the numbers represent the number of reflexions), and at the left of C bands due to beams 3 and 4 alone. By the use of a narrow

screen for S it might be possible to cut out beam 2 and to obtain bands due to 1 and 3, the spacing here being a little less than for 1 and 2.\*

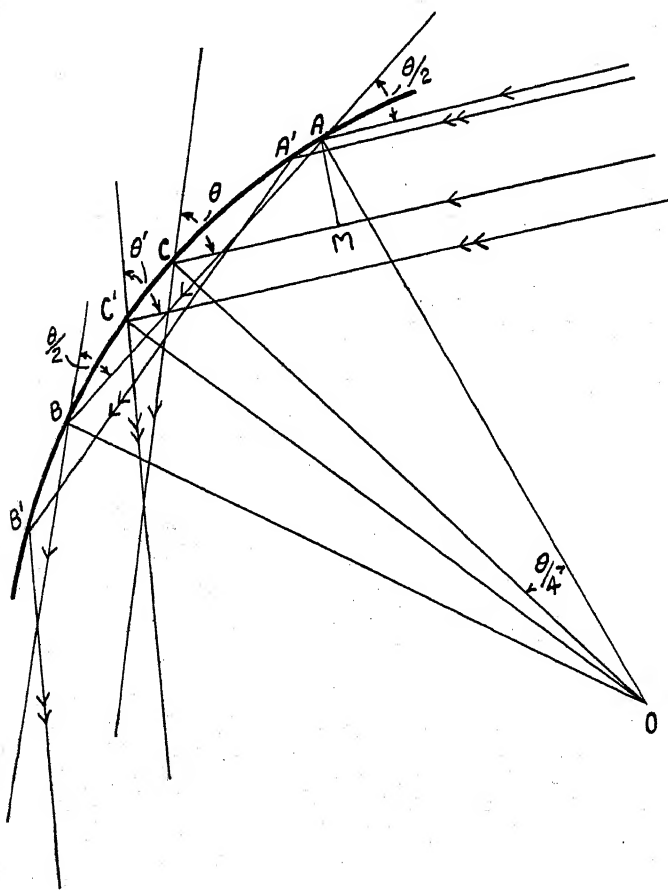


Fig. 1.

If the spectrometer table is rotated, its axis being assumed to touch the reflecting sphere, the positions of the bands do not change, but the intensities of various parts of the pattern do, and certain interferences may be introduced, while others are cut out as the result of the

\*The use of a screen may introduce considerable modifications owing to diffraction effects.

changes in the limits between which  $\theta$  must lie, the determination of these limits being made as described in the next section.

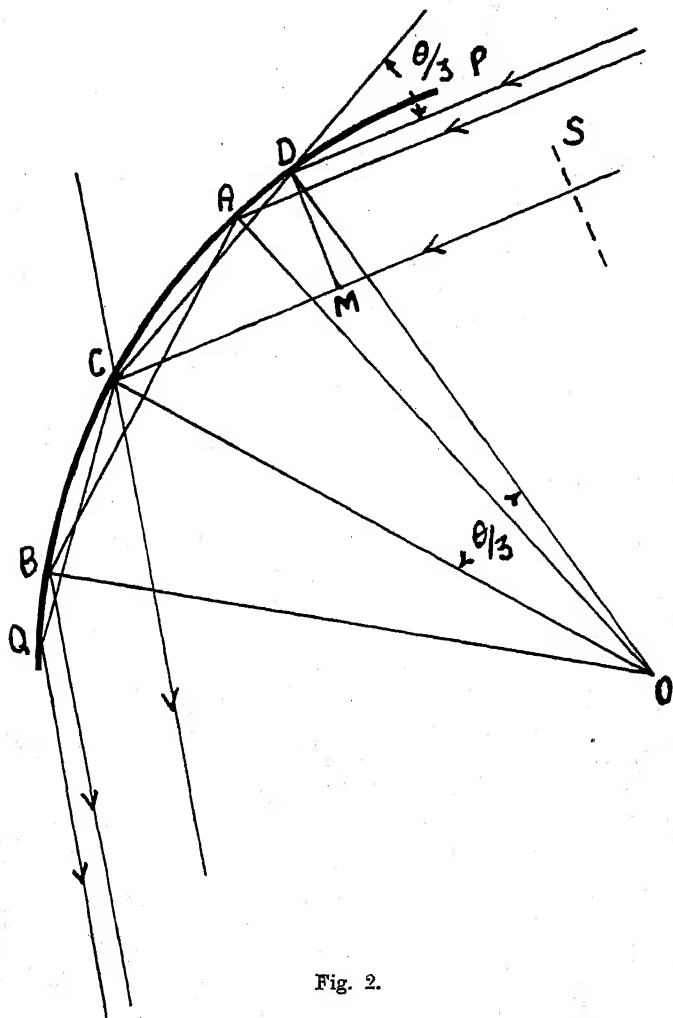


Fig. 2.

## 2. CONDITIONS FOR THE OCCURRENCE OF INTERFERENCE.

If upon the whole of the mirror there fall a beam of parallel light some portion, at least, of this will be reflected

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once, and once only, whatever the value of the angle of incidence,  $i$ , at the centre of the mirror. For interference to occur the values of  $i$  and of  $2\varphi$ , the aperture of the mirror, must be such that the light incident on some portion of the mirror is reflected twice or more times. For a given value of  $\varphi$  the value of  $i$  must exceed a certain minimum value, which is greater the higher the order of the beam, that is the greater the number of reflexions occurring.

The minimum value of  $i$  permitting two reflexions is such that a ray incident at the edge P (Fig. 2 or 3) after reflexion meets the mirror at the other edge Q, being deviated at each reflexion through an angle  $\theta/2$ , where  $\theta$  is the deviation produced by the single reflexion of a parallel incident ray at the centre of the mirror.

If  $i'$  is the angle of incidence at P,

$$i' = i + \varphi$$

$$\text{and } i + \frac{\theta}{2} = \frac{\pi}{2}$$

$$i' + \frac{\theta}{4} = \frac{\pi}{2}$$

$$\text{so that } i = \frac{\pi}{2} - 2\varphi.$$

If the mirror be turned so that  $i$  exceed this value, rays falling on a finite portion of the mirror undergo two reflexions.

In like manner it can be shown that for three reflexions to be possible for some portion of the incident light the minimum value of  $i$  is

$$\frac{\pi}{2} - \frac{3\varphi}{2},$$

for four reflexions it is

$$\frac{\pi}{2} - \frac{4\varphi}{3},$$

and for  $n$

$$\frac{\pi}{2} - \frac{n\varphi}{n-1}.$$

If  $i$  is only slightly greater than one of these critical values the amplitude of the corresponding beam is small compared with those of lower orders, because only a very small portion of the mirror can be effective and interference effects associated with this beam are of small intensity. This is discussed more fully in Section 5.

The limit, for an infinite number of reflexions, gives

$$i = \frac{\pi}{2} - \varphi$$

that is the beam is tangential to the mirror at P, and any further rotation of the mirror involves a departure from the condition stated in the first line of this section, as portion of the mirror is in shadow, so that the effective value of  $\varphi$  is reduced to  $\varphi' = \varphi - \beta$ , where  $\beta$  is the amount of rotation beyond this limiting tangential position. The centre of the illuminated portion of the mirror remains fixed as  $\beta$  is increased, so that  $i$  has the constant value  $\frac{\pi}{2} - \varphi$ , but, as  $\beta$  increases, the multiply reflected beams successively disappear in descending order because  $\varphi'$  is reduced. Thus for the beam of third order to disappear we have

$$i = \frac{\pi}{2} - \frac{3\varphi'}{2}$$

i.e.  $\frac{\pi}{2} - \varphi = \frac{\pi}{2} - \frac{3(\varphi - \beta)}{2}$

$$\text{so that } \beta = \frac{\varphi}{3};$$

for values of  $\beta$  in excess of this only beams of the first and second order occur.

In general, if  $\beta = \frac{\varphi}{n}$ , beams of the  $n$ th and higher orders are not present. If  $\beta = \varphi$ , of course no portion of the mirror is illuminated.

### 3. LIMITS WITHIN WHICH INTERFERENCE EFFECTS MAY BE OBSERVED.

The limits between which lie the deviations associated with a reflected beam of any order permitted by definite values of  $i$  and  $\varphi$  are readily calculated.

In the case of two reflexions the maximum deviation,  $\theta_2$ , is that of the ray for which the second reflexion occurs at the edge Q of the mirror (Fig. 3).

If  $i'$  is the angle of incidence of this ray

$$i' = i + \alpha$$

$$i' + \frac{\theta_2}{4} = \frac{\pi}{2} = i + \alpha + \frac{\theta_2}{4}$$

$$\varphi + \alpha = \frac{\theta_2}{2},$$

$$\text{so that } \theta_2 = \frac{2}{3}\{\pi - 2(i - \varphi)\}.$$

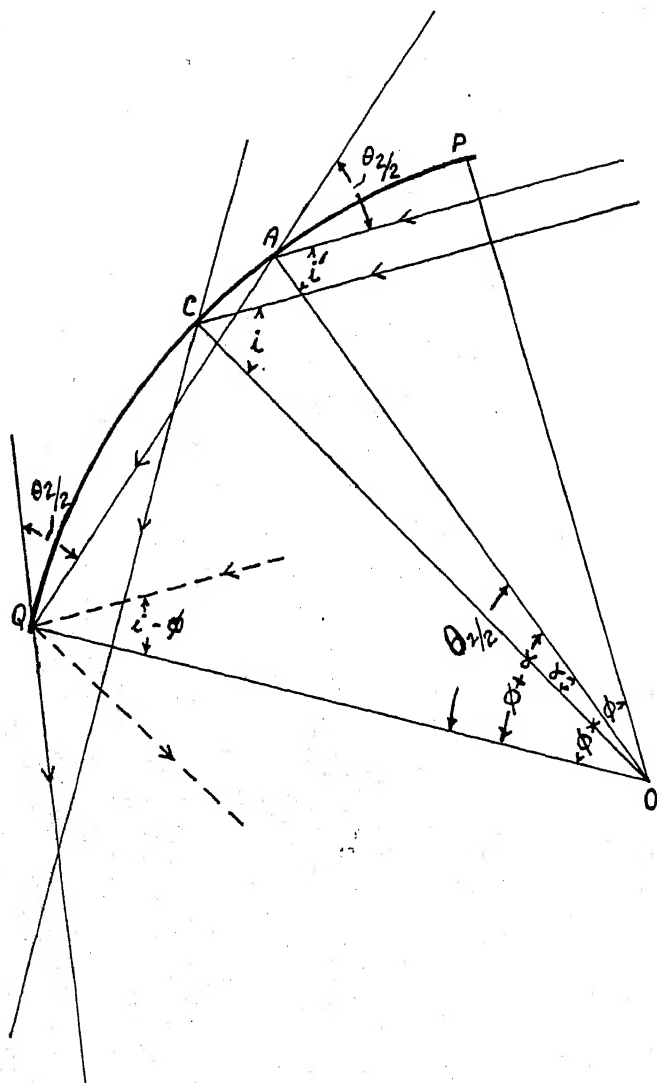


Fig. 3.

The maximum deviation,  $\theta_1$ , for a once reflected beam, is that of the ray incident at Q.

$$\frac{\theta_1}{2} + i - \varphi = \frac{\pi}{2}$$

$$\text{so } \theta_1 = \pi - 2(i - \varphi) = \theta_0 + 2\varphi,$$

where  $\theta_0 = \pi - 2i$ , is the deviation produced on a parallel ray reflected once at the centre of the mirror.

We have, therefore, the maximum deviation for a twice reflected ray

$$\theta_2 = \frac{2}{3}\theta_1 = \frac{2}{3}\{\pi - 2(i - \varphi)\}.$$

Similarly  $\theta_3$ , the maximum deviation of a thrice reflected ray, is that for the ray making its third reflexion at Q, and in this case it is readily shown that

$$\theta_3 = \frac{3}{5}\theta_1,$$

and for a ray reflected  $n$  times the maximum deflection is

$$\theta_n = \frac{n}{2n-1}\theta_1.$$

The method of determining the lower limits of  $\theta$  for a given order is illustrated in the case of a twice reflected beam.

Consider rays incident at points between A and P (Fig. 3). As we go from A we have rays twice reflected, the deviation becoming less as the distance from A increases. The lower limit is attained when we arrive at a point where three reflexions occur (D, Fig. 2), or at the edge of the mirror if the value of  $i$  does not permit three reflexions.

In the former case the lower limit for two reflexions is for the incident ray meeting the mirror just below D, Fig. 2, and the minimum value  $\theta'_2$  is obviously  $\frac{2}{3}\theta_3$ ,  $\theta_3$  being the maximum deviation possible for a thrice reflected ray, so that if three reflexions are possible the minimum deviation of a twice reflected ray is

$$\theta'_2 = \frac{2}{3}\theta_3 = \frac{2}{5}\theta_1$$

$$\text{where } \theta_1 = \pi - 2(i - \varphi).$$

Should three reflexions not be possible, the minimum deviation for a twice reflected ray is that of the ray incident at P for which

$$i' = i + \varphi$$

$$\text{and as } i' + \frac{\theta'_2}{4} = \frac{\pi}{2} = i + \varphi + \frac{\theta'_2}{4}$$

$$\theta'_2 = 2\{\pi - 2(i + \varphi)\}.$$

By similar methods it can be shown that the minimum deviation of a thrice reflected beam is

$$\theta'_3 = \frac{3}{4}\theta'_2 = \frac{3}{7}\theta_1$$

$$\text{or } 3\{\pi - 2(i + \varphi)\}$$

according as there can or cannot be a four times reflected ray.

In general the minimum deviation for a beam reflected  $n$  times is

$$\theta'_n = \frac{n}{2n+1}\theta_1$$

if a ray reflected  $n+1$  times can occur, and

$$\theta'_n = n\{\pi - 2(i + \varphi)\} \text{ if it cannot.}$$

In Table 1, the second column gives the condition for the occurrence of a beam of given order, the third, the

TABLE 1.  
*Critical Angles and Deviation Limits.*

| Order. | Minimum Value of $i$ .                 | Maximum Deviation.       | Minimum Deviation.                                      |
|--------|--|--------------------------|---|
| 1      | —                                      | $\theta_1$               | $\frac{1}{3}\theta_1$ or $\pi - 2(i + \varphi)$         |
| 2      | $\frac{\pi}{2} - 2\varphi$             | $\frac{2}{3}\theta_1$    | $\frac{2}{5}\theta_1$ „ $2\{\pi - 2(i + \varphi)\}$     |
| 3      | $\frac{\pi}{2} - \frac{3}{2}\varphi$   | $\frac{3}{5}\theta_1$    | $\frac{3}{7}\theta_1$ „ $3\{\pi - 2(i + \varphi)\}$     |
| 4      | $\frac{\pi}{2} - \frac{4}{3}\varphi$   | $\frac{4}{7}\theta_1$    | $\frac{4}{9}\theta_1$ „ $4\{\pi - 2(i + \varphi)\}$     |
| ....   | .....                                  | .....                    | .....   |
| $n$    | $\frac{\pi}{2} - \frac{n}{n-1}\varphi$ | $\frac{n}{2n-1}\theta_1$ | $\frac{n}{2n+1}\theta_1$ or $n\{\pi - 2(i + \varphi)\}$ |

maximum deviation, while the fourth and fifth give the lower limits for the two cases. Column four is to be taken except for the beam of the highest order permitted, or more simply the greater of the two values is to be taken.

As an illustration, let  $\phi = 5^\circ$ , the critical angle  $i$  for beam 2 is  $80^\circ$ , for beam 3,  $82^\circ\frac{1}{2}$ , for beam 4,  $83^\circ\frac{1}{2}$ , etc. If the mirror be placed so that  $i = 83^\circ$  we shall have beams 1, 2 and 3, but not beam 4 or others of higher order.

In this case the values of  $\theta$  for the various beams are

|   | Maximum.              | Minimum.<br>(The greater to be taken.)                |
|---|-----------------------|---|
| 1 | $24^\circ$            | $8^\circ$ or $4^\circ$                                |
| 2 | $16^\circ$            | $9^\circ\frac{3}{5}$ „ $8^\circ$                      |
| 3 | $14^\circ\frac{2}{5}$ | $10^\circ\frac{2}{7}$ „ $12^\circ$                    |
| 4 | $13^\circ\frac{5}{7}$ | $10^\circ\frac{2}{3}$ „ $16^\circ$ , i.e. min. > max. |

An examination of Table 1 shows that the ends of the system of interference bands consist of bands due to beams 1 and 2. If beams of the third or higher order are present, these end sections cover the ranges  $\frac{2}{3}\theta_1$  to  $\frac{3}{5}\theta_1$  and  $\frac{3}{7}\theta_1$  to  $\frac{2}{5}\theta_1$ . When  $i = \frac{\pi}{2} - \phi$ ,  $\theta_1 = 4\phi$  and these ranges amount to  $\frac{4\phi}{15}$  and  $\frac{4\phi}{35}$  respectively.

If  $i$  has the value which just eliminates beam 3, that is  $i = \frac{\pi}{2} - \frac{3}{2}\phi$  we have interference bands due to beams 1 and 2 alone over the range  $\frac{2}{3}\theta_1$  to  $\frac{2}{5}\theta_1$  or  $\frac{4}{15}\theta_1$ . In this case  $\theta_1$  is  $5\phi$ , so the bands extend over a range of  $\frac{4}{3}\phi$ .

Bands due to beams 1 and 2, undisturbed by other beams, can also be obtained over a wide range by rotating the mirror beyond the position giving the beam of infinite

order until the shadowing effect prevents the occurrence of any but beams 1 and 2. As shown earlier (Section 2), we must have  $\beta = \frac{\varphi}{3}$  so that  $\varphi' = \frac{2\varphi}{3}$  and applying the results of Table 1 with  $i = \frac{\pi}{2} - \varphi$  and  $\theta_1 = \pi - 2(i - \varphi') = \frac{10\varphi}{3}$  we have beam 2 extending from  $\frac{20\varphi}{9}$  to  $\frac{4\varphi}{3}$ , that is over a range of  $\frac{8\varphi}{9}$ .

This is less than the above value of  $\frac{4\varphi}{3}$ , but for purposes of measurement this arrangement is more suitable, because the values of  $\theta$  are less, and, as is shown in the next section, the bands are further apart, so that a wider collimator slit is permissible, and the path difference of the interfering rays is smaller, so that any departure from homogeneity in the light is less important.

It must be noted that in practice the bands are of imperceptible intensity near the ends of the theoretical ranges because of the very small area of the mirror contributing to one of the beams.

The photograph F, Plate VII, has been obtained with the mirror placed in the second position described above, portion being in shadow so that beams of order higher than 2 do not occur.

In this discussion it is assumed that the effects are observed through a telescope focussed for parallel rays. If the telescope is not used, the bands being observed with the aid of an eye-piece or photographic plate, the modifications in these expressions are small if the distance from the mirror is great; for example, if the eye-piece is focussed on the second focal line at a distance from the mirror  $\frac{R}{2 \cos i}$ ,  $i$  being a large angle.

#### 4. THE DISTANCE BETWEEN ADJOINING INTERFERENCE BANDS.

##### (a) Bands due to beams 1 and 2.

Assuming in this and in the other cases that observations are made with a telescope focussed for parallel rays, the path difference is  $AB - 2CM$  (Fig. 1).

$$P_2 = AB = 2R \sin \theta/4 = 4R \sin \theta/8 \cos \theta/8$$

$$P_1 = 2CM = 2CA \cos ACM = 4R \sin \theta/8 \cos 3\theta/8$$

$$\Delta_{21} = P_2 - P_1 = 4R \sin \theta/8 (\cos \theta/8 - \cos 3\theta/8) \\ = 16R \sin^3 \theta/8 \cos \theta/8 = R\theta^3/32.$$

If  $\theta$  is altered by a small amount  $\delta\theta$ , the change in path difference is

$$\delta\Delta_{21} \doteq \frac{3}{32} R\theta^2 \delta\theta$$

and if  $\delta\theta_\lambda$  is the angular spacing of two consecutive bands

$$\delta\theta_\lambda \doteq \frac{32}{3} \frac{\lambda}{R\theta^2}.$$

(b) Bands due to beams 1 and 3.

In this case, Fig. 2, we have

$$P_1 = 2CM = 2CD \cos DCM = 4R \sin \theta/6 \cos \theta/3$$

$$P_3 = 2DC = 4R \sin \theta/6$$

$$\therefore \Delta_{31} = P_3 - P_1 = 4R \sin \frac{\theta}{6} \left(1 - \cos \frac{\theta}{3}\right)$$

$$= 8R \sin^3 \frac{\theta}{6} \doteq \frac{R\theta^3}{27}$$

$$\delta\Delta_{31} \doteq \frac{R\theta^2}{9} \delta\theta$$

$$\delta\theta_\lambda \doteq 9 \frac{\lambda}{R\theta^2}.$$

(c) Bands due to beams 1 and 4.

$$\text{Here } \Delta_{41} = 2R \left(4 \sin \frac{\theta}{8} - \sin \frac{\theta}{2}\right)$$

and putting  $\sin \theta = \theta - \frac{\theta^3}{6}$ , we have

$$\Delta_{41} \doteq \frac{5}{128} R\theta^3$$

$$\delta\Delta_{41} \doteq \frac{15}{128} R\theta^2 \delta\theta$$

$$\delta\theta_\lambda \doteq \frac{128}{15} \frac{\lambda}{R\theta^2}.$$

(d) Bands due to beams 1 and 5.

$$\Delta_{51} = 4R \sin \frac{\theta}{10} \left(2 - \cos \frac{\theta}{5} - \cos \frac{2\theta}{5}\right)$$

taking  $\cos \theta = 1 - \frac{\theta^2}{2}$

$$\Delta_{51} \doteq \frac{1}{25} R\theta^3$$

$$\text{giving } \delta\Delta_{51} \doteq \frac{3}{25} R\theta^2 \delta\theta$$

$$\text{and } \delta\theta \doteq \frac{25}{3} \frac{\lambda}{R\theta^2}.$$



In the limiting case of incident and emergent beams being tangential to the mirror, we have

$$\Delta_{\infty 1} = 2R \left( \frac{\theta}{2} - \sin \frac{\theta}{2} \right) \\ \div \frac{1}{24} R\theta^3.$$

Of course bands due to beam 1 and a beam of order higher than 2 are complicated by the presence of other beams, certainly all intervening beams, unless these are stopped by appropriate screening. This is discussed in Section 6.

By the use of suitable screens we can obtain bands corresponding to any pair of the beams permitted by the values of  $i$  and  $\varphi$ ; the path differences and beam separations are readily determined from the results already given.

For example, if we are concerned with the bands due to beams 3 and 4, we have

$$\Delta_{43} = \Delta_{41} - \Delta_{31} = \left( \frac{5}{128} - \frac{1}{27} \right) R\theta^3 \\ = \frac{7}{27 \times 128} R\theta^3 \\ \text{and } \delta\theta_\lambda = \frac{9 \times 128}{7} \cdot \frac{\lambda}{R\theta^2}.$$

In Table 2 numbers proportional to the path differences  $\Delta$  and the band separations  $\delta\theta$  are given for various

TABLE 2.

| Band. | $\frac{\Delta}{R\theta^3}$ | $\delta\theta_\lambda \frac{R\theta^2}{\lambda}$ |
|-------|----------------------------|--|
| 2-1   | 0.0312                     | 10.67  |
| 3-1   | 370                        | 9.00   |
| 4-1   | 390                        | 8.53   |
| 5-1   | 400                        | 8.33   |
| 3-2   | .0058                      | 58   |
| 4-2   | 78                         | 43   |
| 5-2   | 88                         | 38   |
| 4-3   | .0020                      | 165  |
| 5-3   | 30                         | 112  |
| 5-4   | .0010                      | 355  |

pairs of beams. In the case of bands due to interference between beams of high order, that is for the lower part of the table, the numerical values are untrustworthy, because the approximations to the trigonometrical functions might not be justified for these small path differences. The numbers in the last column, however, serve for the recognition of any particular set of bands.

The distance between successive bands due to any pair of beams is determined as in the instances already given. Thus for the 4-3 bands we have

$$\begin{aligned}\Delta_{43} &= \frac{7}{27 \times 128} R \theta^3 \\ \delta \Delta_{43} &= \frac{7}{9 \times 128} R \theta^2 \delta \theta \\ \text{and } \delta \theta_{\lambda} &= \frac{9 \times 128}{7} R \theta^2 \delta \theta_{\lambda}.\end{aligned}$$

#### 5. RELATIVE INTENSITIES OF MAXIMA AND MINIMA IN A BAND SYSTEM.

One factor affecting this is the homogeneity of the light used. If, as in the photographs given here, the yellow doublet of sodium is employed, the interference effects will be least marked when the path difference of the interfering rays is about  $500\lambda$  or any odd multiple of this. In the observations given in Table 3, for the maximum value of  $\theta$  the path difference is about  $400\lambda$ , and the bands here were found to be less sharp than for smaller path differences. The change of phase at reflexion, occurring more often for one beam than for the other, and depending on the angle of incidence, naturally has an influence on the position of maximum sharpness.

A third and usually most important factor affecting the intensity of the interference effects is that of the relative areas of the mirror effective in the production of the two interfering beams. Let us consider first the case in which the collimator slit is replaced by a single luminous point, and let  $ab$  (Fig. 4) be the points of incidence of two singly reflected rays for which the deviations are  $\theta$  and  $\theta + \delta\theta$ , where  $\delta\theta \ll \delta\theta_{\lambda}$ ; let  $cd$  and  $c'd'$  be the points of contact of twice reflected rays giving the same total deviations  $\theta$  and  $\theta + \delta\theta$ . These incident and reflected rays are supposed all to be in the one plane, the points of contact being on a great circle. Rotate the incident and reflected rays about an axis parallel to the incident beam

and passing through the centre of curvature of the mirror;  $ab$ ,  $cd$  and  $c'd'$  trace out strips as shown, and light falling on the first two is deviated, after one or two reflexions, through angles ranging from  $\theta$  to  $\theta + \delta\theta$ . The light from the central strip converges to form a "vertical" line close to the mirror. The rays from this, the first focal line, converge on to the second focal line, and in the absence of a telescope give a finite bright illuminated line on the axis of rotation. By suitable focussing of the telescope a similar line is obtained, or, if it is focussed for parallel

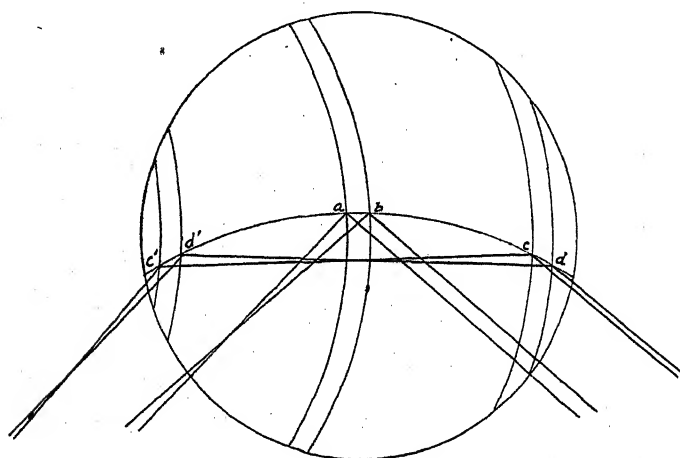


Fig. 4.

rays, a horizontal bright band, the brightness in each case depending on the height of the strips of the mirror through  $ab$ .

The twice reflected beam, alone, gives a similar line or band, the two reflexions compensating the larger angle of incidence, but the brightness is less because less of the incident beam contributes to it. The height of one at least of the strips through  $cd$ ,  $c'd'$  must be less than that through  $ab$  and the effective height is obviously the smaller of these.\* Further, the amount of light incident on a

---

\* If the diameter of the collimated beam is less than that of the mirror, the differences of strip heights may be relatively small.

given height of the strip  $cd$  is less than on an equal height of the strip  $ab$ .

$$ab = \frac{1}{2} R \delta \theta$$

$$cd = \frac{1}{4} R \delta \theta$$

$$c'd' = \frac{3}{4} R \delta \theta$$

so the amount of light falling on equal heights of the strips  $ab$  and  $cd$  are in the ratio of  $\frac{1}{2} R \delta \theta \cos i_1$ , to  $\frac{1}{4} R \delta \theta \cos i_2$ ,

where  $i_1$  and  $i_2$  are the angles of incidence at  $a$  and  $c$ . As  $\cos i_1 = \sin \frac{\theta}{2}$  and  $\cos i_2 = \sin \frac{\theta}{4}$  this ratio is  $\sin \frac{\theta}{2} : \frac{1}{2} \sin \frac{\theta}{4}$ ,

or approximately 4 : 1, and, if the effective heights were equal and no other factors entered, the ratio of maximum to minimum intensity in the bands would be  $\frac{25}{9}$ . On

account of the difference in height the ratio would be less than this, but other factors have to be taken into account. There is a loss at each reflexion, and here one beam is reflected once and the other twice; but the coefficient of reflexion is not the same for each beam, depending on the angle of incidence, this last factor favouring the more frequently reflected beam.

Without discussing these points further at this stage, it is readily seen that the nearer one of the strips  $cd$   $c'd'$  is to the edge of the mirror, the smaller the amplitude of the beam concerned, and the less marked the interference effects due to it. Similar considerations hold concerning the effectiveness of multiply reflected beams, the intensity decreasing as the order increases.

Each point on the slit, being the origin of a parallel incident beam, is responsible for the like effect of an illuminated length upon the corresponding second focal line. These focal lines are convergent, being radii of the sphere parallel to the collimated beams from the various points of the slit, so that in the plane containing the second focal lines we have a system of interference bands, the band height being proportional to the distance from the centre of the sphere, that is greatest for that part of the pattern corresponding to the least deviated rays.

In E and F, Plate VII, the whole pattern photographed is shown. Here the height is least for the least deviated

portion because the plate was perpendicular to the rays from the mirror, the least deviated part being nearly on the plane of the focal lines and the other end beyond that plane. In the other photographs on the Plate, only a central horizontal strip of the pattern is given.

## 6. SUPERPOSITION OF MORE THAN TWO BEAMS.

The general expression for the resultant amplitude when we have several beams is

$$A = a_1 + a_2 \cos \frac{\alpha}{32} + a_3 \cos \frac{\alpha}{27} + a_4 \cos \frac{5\alpha}{128} + a_5 \cos \frac{\alpha}{25} + \dots$$

where  $\alpha = \frac{2\pi}{\lambda} R\theta^3$  and  $a_1, a_2$ , etc., represent the amplitudes of the beams, depending on the factors just discussed. Generally these amplitudes are in descending order of magnitude, unless screens are used as described earlier. They are functions of  $\theta$ , being zero except within the limits given in Table 1, and have a single maximum value somewhere between those limits. In the following discussion it is assumed that we are considering a small portion of the pattern over which the amplitudes  $a_1, a_2$ , etc., are practically constant.

If the first three are present, we have a phenomenon analogous to beats, and the amplitude may be expressed in the form

$$A = a_1 + a \cos \left( \alpha \times \frac{\frac{1}{32} + \frac{1}{27}}{2} + \beta \right)$$

$$\text{where } a^2 = a_2^2 + a_3^2 + 2a_2a_3 \cos \alpha \left( \frac{1}{27} - \frac{1}{32} \right).$$

We have a system of bands of separation slightly different from that observed when beams 1 and 2 alone are effective and the intensity of these varies periodically as a function of  $\alpha$ , that is of  $\theta^3$ , the positions of maximum amplitude being given by  $\alpha \left( \frac{1}{27} - \frac{1}{32} \right) = 2\pi p$ ,  $p$  being an integer, that is

$$\frac{R\theta^3}{\lambda} \left( \frac{1}{27} - \frac{1}{32} \right) = p.$$

If we have beams 1 and 2 alone the positions of maximum amplitude are given by  $\frac{R\theta^3}{\lambda} \cdot \frac{1}{32} = q$ , where  $q$  is an integer,

so that the angle  $\delta\theta'$  for these secondary maxima is related to  $\delta\theta$  for the 1-2 system by the equation

$$\frac{\delta\theta'}{\delta\theta} = \frac{\frac{1}{32}}{\frac{1}{32} - \frac{1}{27}} = \frac{27}{5}.$$

Photograph E, Plate VII, illustrates this effect, and when beam 1 is suppressed we have this system of bands as in the ends of B.

It is to be noted that the spacing of the bands is not a linear function of  $\theta^3$ , as when only two beams interfere, because  $\beta$  is a function of  $\alpha$ , and therefore of  $\theta^3$ .

Instances of other combinations of three interfering beams are similarly treated.

TABLE 3.

| Band Number. | Spectrometer Reading. |    |    | Difference for 10 Bands. |    | Mean $\theta$ . |    |    | $\theta^3 \delta\theta_{\lambda} \times 10^5$ . |
|--------------|-----------------------|----|----|--------------------------|----|-----------------|----|----|---|
|              | °                     | '  | "  | '                        | "  | °               | '  | "  |   |
| 0            | 360                   | 0  | 40 |                          |    |                 |    |    |   |
| 5            | 59                    | 54 | 10 | 13                       | 10 | 17              | 12 | 5  | $3.45 \times 10^5$                              |
| 10           |                       | 47 | 30 | 13                       | 30 |                 | 5  | 25 | .50   |
| 15           |                       | 40 | 40 | 14                       | 0  | 16              | 58 | 30 | .57   |
| 20           |                       | 33 | 30 | 14                       | 30 | 16              | 51 | 25 | .65   |
| 25           |                       | 26 | 10 |                          |    |                 |    |    |   |
|              |                       |    |    |                          |    |                 |    |    | 3.54  |
| 0            | 358                   | 31 | 30 |                          |    |                 |    |    |   |
| 5            |                       | 23 | 20 | 16                       | 10 | 15              | 41 | 25 | 3.53  |
| 10           |                       | 15 | 20 | 16                       | 20 |                 | 33 | 10 | .50   |
| 15           |                       | 7  | 0  | 17                       | 10 |                 | 24 | 45 | .61   |
| 20           | 7                     | 58 | 10 | 17                       | 50 |                 | 16 | 5  | .68   |
| 25           |                       | 49 | 10 |                          |    |                 |    |    |   |
|              |                       |    |    |                          |    |                 |    |    | 3.58  |
| 0            | 355                   | 3  | 0  |                          |    |                 |    |    |   |
| 5            | 4                     | 49 | 40 | 27                       | 20 | 12              | 7  | 20 | 3.55  |
| 10           |                       | 35 | 40 | 28                       | 10 | 11              | 53 | 35 | .53   |
| 15           |                       | 21 | 30 | 29                       | 50 |                 | 38 | 45 | .58   |
| 20           |                       | 5  | 50 | 31                       | 20 |                 | 23 | 50 | .61   |
| 25           | 3                     | 50 | 10 |                          |    |                 |    |    |   |
|              |                       |    |    |                          |    |                 |    |    | 3.57  |

Mean value of  $\theta^3 \delta\theta_{\lambda} = 3.56 \times 10^{-5}$ .

$$\lambda = \frac{3}{32} R \theta^3 \delta\theta_{\lambda} = 5.95 \times 10^{-5} \text{ cm.}$$

## 7. DETERMINATION OF WAVE-LENGTH OF LIGHT.

Visual observations were made of the positions of bands produced by beams 1 and 2 under conditions for which no other interferences could take place, the mirror being rotated when necessary to satisfy these. Results are recorded in Table 3 which are of interest, inasmuch as the method lends itself as a class exercise in determining wave-lengths, which is much less troublesome than that with Fresnel biprism or mirrors.

The mirror used was a stainless steel one of radius of curvature 17.9 cms. and diameter 5 cms. The spectrometer was a student's type instrument with an 8 inch circle by which readings to 10" could be made. Here the telescope, focussed for parallel rays, was used for determining the band positions. The bands in the various groups of readings are counted from some arbitrary zero. The spectrometer reading for no deviation was  $342^{\circ} 42' 0''$ .

No special care was taken in making these readings, none being repeated. The value of  $\theta$  taken was the mean of the values at the beginning and end of each set of ten bands, which is here a sufficiently close approximation. By measuring the more widely spaced bands in a photograph such as F in Plate VII, much higher accuracy should

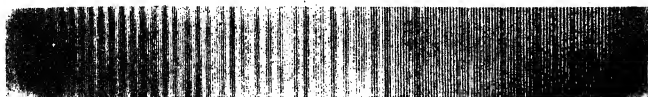
TABLE 4.

| Band No. | Telescope Reading. |    |    |      |    |    | Mean $\theta$ . |    |    | $\theta^2 \delta \theta_{\lambda} \times 10^4$ |
|----------|--------------------|----|----|------|----|----|-----------------|----|----|--|
|          | °                  | '  | "  |      | '  | "  | °               | '  | "  |  |
| 0        | 360                | 23 | 10 | 0-4  | 28 | 0  | 17              | 27 | 10 | 1.90   |
| 1        |                    | 16 | 0  | 1-5  | 28 | 40 |                 | 19 | 40 | .90  |
| 2        |                    | 9  | 20 | 2-6  | 28 | 20 |                 | 13 | 0  | .86  |
| 3        |                    | 2  | 20 | 3-7  | 29 | 30 |                 | 5  | 35 | .90  |
| 4        | 59                 | 55 | 10 | 4-8  | 30 | 10 | 16              | 58 | 5  | .92  |
| 5        |                    | 47 | 20 | 5-9  | 29 | 50 |                 | 50 | 25 | .88  |
| 6        |                    | 40 | 40 | 6-10 | 30 | 30 |                 | 43 | 30 | .88  |
| 7        |                    | 32 | 50 |      |    |    |                 |    |    |  |
| 8        |                    | 25 | 00 |      |    |    |                 |    |    |  |
| 9        |                    | 17 | 30 |      |    |    |                 |    |    |  |
| 10       |                    | 10 | 20 |      |    |    |                 |    |    |  |

Mean value of  $\theta^2 \delta \theta_{\lambda} = 1.89 \times 10^{-4}$ .

$$\lambda = \frac{5}{9 \times 32} R \theta^2 \delta \theta_{\lambda} = 5.87 \times 10^{-5} \text{ cm.}$$

*A*



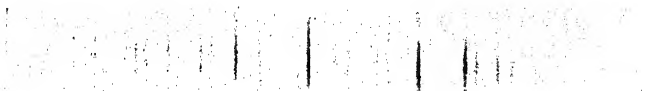
*p*

*q*

*q'*

*p'*

*B*



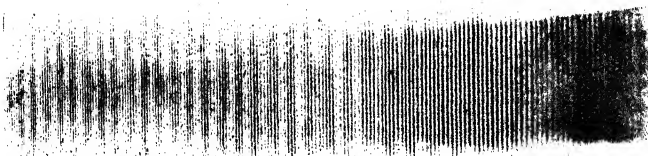
*C*



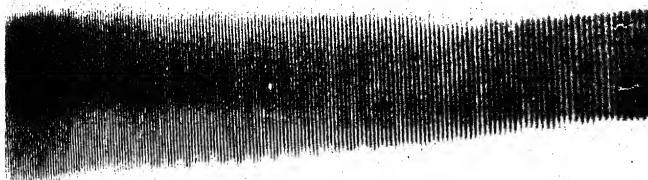
*D*



*E*



*F*







be attained, giving a more trustworthy value of  $\lambda$  if  $R$  and  $\theta$  were measured with corresponding precision.

Measurements with bands due to beams 2 and 3 by screening beam 1 give the results in Table 4.

This result is satisfactory in view of the difficulty in centering the comparatively broad bands. Towards the end of this set of bands it was observed that another system was superposed with spacing about three times that of the 2-3 system. This is due to beam 4 being added, the separation of the 4-3 bands being  $\frac{20}{7}$  times that of the 2-3 system.

### SUMMARY.

Interference bands may be obtained when light is reflected at large angles of incidence from a spherical concave mirror as the result of the superposition of beams which have been reflected different numbers of times. The conditions under which the bands may occur are determined and the ranges over which the various interference systems may be described for a given mirror are evaluated. An investigation is made of the intensities of the various band systems. These bands provide a convenient experiment for a reasonably accurate class determination of the wave-length of light.

### DESCRIPTION OF PLATE.

A. Interference pattern with  $i$  large enough to allow beams of several orders.

At ends bands are due to beams 1 and 2 only; between  $pp'$  beam 3 is also present; between  $q$   $q'$ , beam 4, and in central part beams of higher order occur.

Note greater separation of bands at right where  $\theta$  is least.

B. A screen introduced stopping beam 1, interference bands due to remaining beams appearing. Note the coincidence of maxima in A, B, C and D, for all of which the position of the mirror was the same. Bands due to beams 2-3 at the ends.

C. Screen moved so as to intercept more of the light, bands due to beams 2-3 not appearing in part of the pattern.

D. Screen cuts out all light except that incident on area very near edge of mirror, allowing high orders only.

E. Value of  $i$  altered so that portion of mirror is self-screened, cutting out beams of order higher than 3.

F. Self-screening increased so that bands are due only to beams 1 and 2.

These photographs were taken without any lens between mirror and plate, which were at a distance apart of about 80 cms. The size is the same as in the original plates.

## THE ACTION OF NITROUS ACID ON AMINES.

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(With four text-figures.)

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Despite the importance of the reaction between nitrous acid and the amines, a completely satisfactory explanation of its mechanism is still lacking. It is not an easy reaction to study experimentally, because nitrous acid is an unstable substance, and because the initial products of the reaction often undergo secondary changes with great ease. Much of the earlier experimental work forms an unreliable basis from which to reason. In the last few years, however, careful studies of the kinetics of the reaction with several amines have been undertaken by Taylor (*J. Chem. Soc.*, 1928, 1099 and 1897); Taylor and Price (*J. Chem. Soc.*, 1929, 2052); Abel, Schmid, and Schafranik (*Z. physik. Chemie*, Bodenstein Festband, 1931, 510); and Abel, Schmid and Sidon (*Z. Elektrochemie*, 1933, 39, 863). In all these experiments precautions have been taken to avoid decomposition of nitrous acid, and the conclusion has been reached that ammonium ions or substituted ammonium ions, nitrite ions and nitrous acid are all involved in the reaction. The last-named workers, in addition, have formed the opinion that an intermediate product containing three nitrogen atoms is formed.

The results of a study of the nitrosation of methylaniline in methanol solution by dilatometric and conductimetric methods (Earl and Hall, *J. Chem. Soc.*, 1933, 510) were sufficiently striking to urge a wider application of similar methods. The diazotisation of aniline in methanol solution has now been studied in greater detail than previously (*Jour. R. Soc. N.S.W.*, 1932, 66, 157, 453). The observations indicate that, in spite of the masking effects of the many possible secondary reactions, the course of the initial reaction is the same for methylaniline and aniline. Fig. 1 shows the temperature-volume curves obtained for

reaction mixtures containing the two amines under comparable conditions. The principal features are similar, after eliminating the peak O, which, as previously pointed out, is caused by a spontaneous rise in temperature of the reaction mixture. Fig. 2 shows clearly both the discontinuity in the rate of contraction at constant temperature and also the influence of varying quantities of hydrochloric acid. The effects of temperature on the velocity of the reaction is marked; Fig. 3 is self-explanatory.

Conductivity measurements during diazotisation of aniline in methanol solution (Fig. 4) give good ground for supposing that the later stages of the reaction involve a rapid increase in hydrogen ion concentration; this is more definite when the initial acidity is relatively high and there is presumably less interference by secondary reactions such as the formation of aminoazobenzene.

If the reaction of diazotisation were between anilinium ions and nitrous acid, as accepted by many chemists (cf. Reilly and Drumm, *J. Chem. Soc.*, 1935, 871) the observations here recorded would admit of a similar explanation to that tentatively adduced for the nitrosation of methyl aniline (Earl and Hall, *loc. cit.*). Bearing in mind, however, the conclusions of Taylor and Abel and Schmid and their collaborators (*loc. cit.*), another interpretation of the irregularity of these volume and conductivity changes is permissible. An initial reaction, the velocity of which is accelerated by increased hydrogen ion concentration, and which does not bring about much change in the volume of the reaction mixture, may proceed until a critical concentration of the first reaction product is reached. The latter may then commence to decompose, liberating hydrogen ions and bringing about a rapid decrease in volume and increase in conductivity. This explanation would allow the existence of the intermediate stage which Abel and Schmid believe to occur.

A factor which may be involved in the experiments here described and for which no allowance has been made is the methyl nitrite/nitrous acid equilibrium which must exist when using nitrous acid in methanol solution. A satisfactory technique for working with aqueous solutions has not yet been devised, because the reaction velocities involved are obviously much greater.

The essential similarity of all nitrous acid-amine reactions has been pointed out by Kenner and Adamson (*J. Chem.*

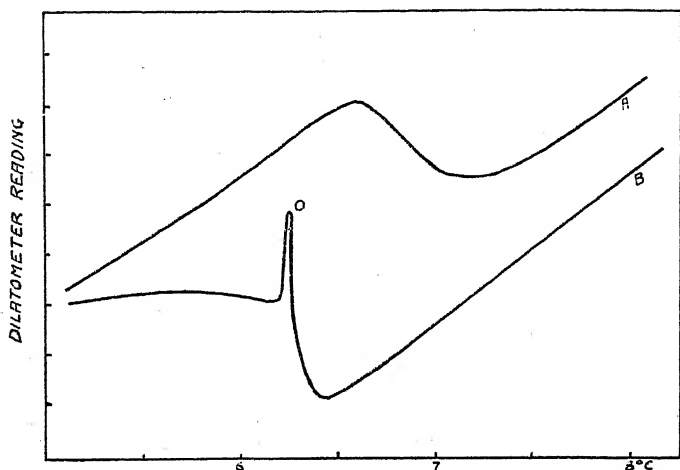


Fig. 1. A. Aniline hydrochloride (1 mol.), sodium nitrite (1 mol.) and hydrochloric acid.  
 B. Methylaniline hydrochloride (1 mol.), sodium nitrite (1 mol.) and hydrochloric acid.

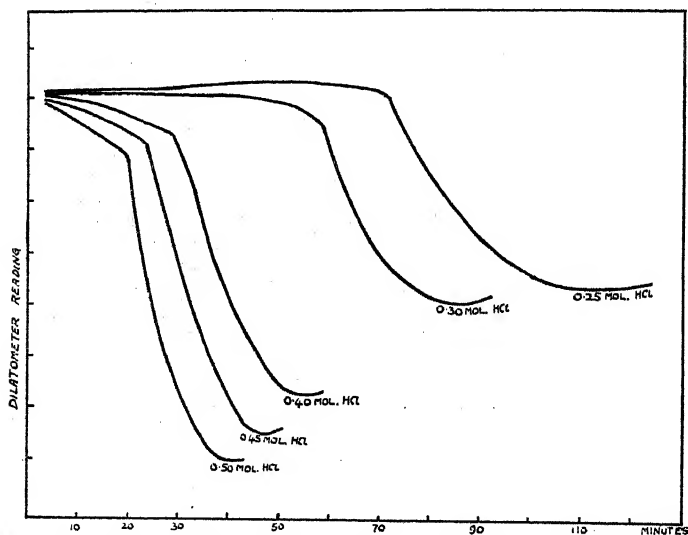


Fig. 2. Sodium nitrite (1 mol.), aniline hydrochloride (1 mol.) and hydrochloric acid. Temperature:  $9.5^{\circ}\text{C}$ .

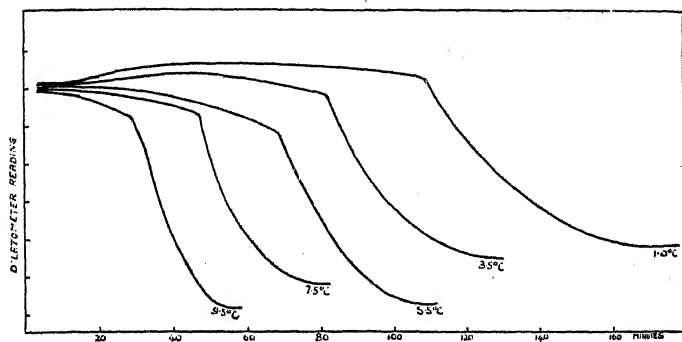


Fig. 3. Sodium nitrite (1 mol.), aniline hydrochloride (1 mol.) and hydrochloric acid (0.4 mol.).

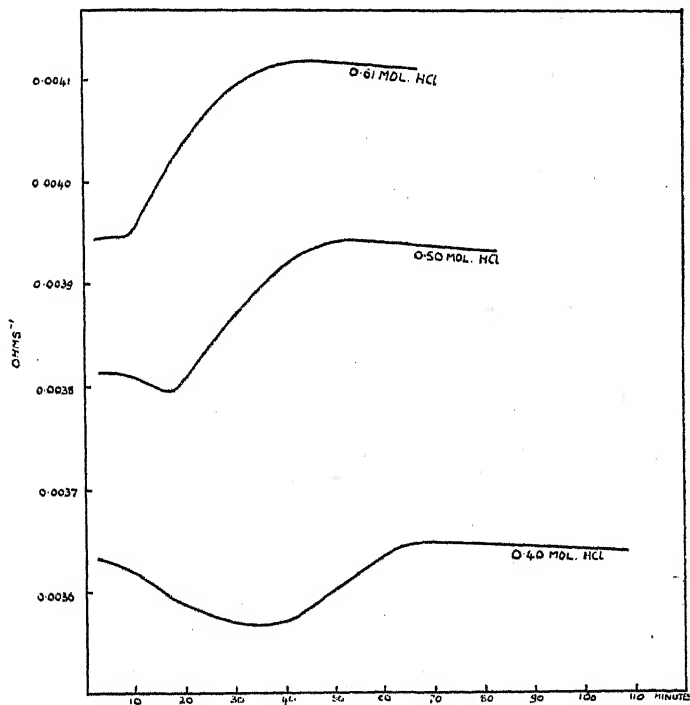


Fig. 4. Conductivity. Sodium nitrite (1 mol.), aniline hydrochloride (1 mol.) and excess hydrochloric acid.

*Soc.*, 1934, 838), who suggested a general theoretical explanation of the mechanism. It is difficult, however, to bring this explanation into line with the experimental evidence for the formation of an intermediate substance, and the increasing hydrogen ion concentration towards the end of the reaction.

#### EXPERIMENTAL.

The technique used in this investigation was similar to that previously described (Earl and Hall, *Jour. R. Soc. N.S.W.*, 1932, 66, 157, 453; *J. Chem. Soc.*, 1933, 510).

The actual concentrations of the solutions upon which the various curves were based were as follows:

Fig. 1.—1.180 gms. aniline, 0.875 gms. sodium nitrite and 0.693 gms. hydrochloric acid in 60 cc. methanol; 1.358 gms. methyl aniline, 0.875 gms. sodium nitrite and 0.693 gms. hydrochloric acid in 60 cc. methanol.

Fig. 2.—2.071 gms. aniline hydrochloride, 1.104 gms. sodium nitrite and various proportions of hydrochloric acid as indicated, in 60 cc. methanol.

Fig. 3.—Similar concentrations to those used for Fig. 2.

Fig. 4.—0.259 gms. aniline hydrochloride and 0.138 gms. sodium nitrite in 45 cc. methanol, with various proportions of hydrochloric acid as indicated. The cell used was the same as that described previously (*J. Chem. Soc.*, 1933, 510).

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EVIDENCE OF MAGMATIC STOPING IN A DYKE AT  
HARTLEY, N.S.W.

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(With two text-figures.)

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## INTRODUCTION.

The dyke examined is situated behind McGarry's Royal Hotel, Por. 1, Parish of Hartley, County of Cook. It occurs in the bed of a small creek which runs parallel to the Main Western Road, and which, near the dyke, turns north to join the River Lett. The position of this dyke is marked on two published maps.<sup>(2) (4)</sup>

An interesting feature of this small intrusion is the irregularity of its margins, and as a result of an examination of these we present what we consider to be evidence of magmatic stoping.<sup>(3)</sup>

## FIELD OCCURRENCE.

Basic dykes of this type are very numerous in the Hartley District, and their petrology will be the subject of a later publication by one of us (G.A.J.).

The dykes consist of deuterically altered dolerites, and are intrusive into granites and diorites and the hornfelses of their contact-zones.

The dyke in question invades granite, and outcrops in the creek bed over a length of fifty-eight feet. A small isolated outcrop, measuring about four feet in length, occurs thirty-one feet downstream. The dyke dips W. 21° S. at 69°, and its average width is four and a half feet.

There is a waterfall about seven feet in height at the southern end of the dyke, and the dolerite is exposed in its steep face. Downstream from the waterfall the creek flows along the western margin of the dyke. The creek



thus partly conceals the exact nature of the dolerite-granite boundary, but so far as can be seen it follows almost a straight-line course along the major jointing in the granite (see Fig. 1), although "side-stepping" of small amount is possible.\* At first sight the eastern margin appears to be much more irregular than is actually the case. This is due to the irregular erosion of the dolerite and granite, the western margin being on a more even erosion surface. The intersection of the dipping dyke with the rugged and rounded surfaces of the granite gives rise to an irregular margin on the east.

On looking down into the creek bed from above the eastern bank, it is evident that the only irregularities are those produced by minor "side-stepping" along joints in the granite (see Fig. 1).

#### EVIDENCE OF STOPING.

The following observations seem to indicate that magmatic stoping has played a part in the emplacement of this dyke.

##### (i) Jointing.

In the immediate vicinity of the dyke the following joint-directions are prevalent in the granite: N. 21° W., N. 31° W., N. 13° W., N. 38° W., N. 15° E., N. 32° E.

The dyke trends along the major joint N. 21° W., but towards the northern end bends to conform with the direction N. 31° W., which here has become dominant.

Reference to Fig. 1 will show the "side-stepping" along the minor joints on the eastern side and the closeness of the major joint-fissures trending N. 21° W.

At the northern extremity of the mass where the dyke narrows, the jointing of the granite is more complex, and transverse joints prevent the intrusion from following its normal course.

##### (ii) Vein.

The detached outcrop at the northern end of the dyke shows the interesting feature of an angular mass of granite almost entirely surrounded by dolerite. A narrow vein of dolerite about two inches wide occupies a joint-fissure on the western side and the main mass narrows to about a foot on the eastern side of the granite block.

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\* The survey was carefully made with compass and tape, and may be regarded as reasonably accurate.

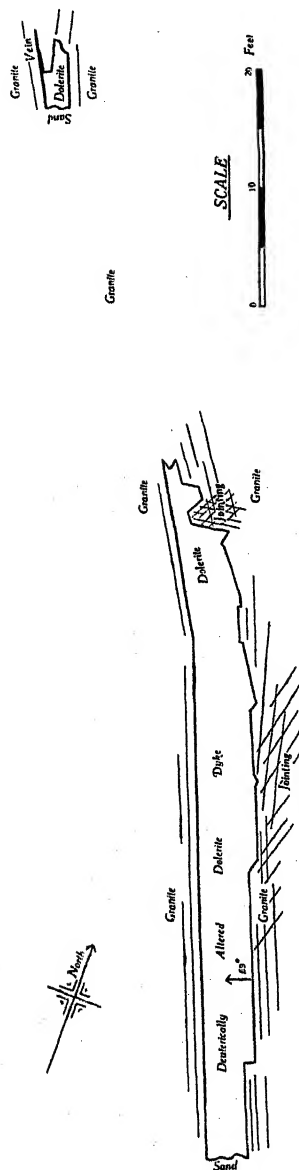


Fig. 1. Map of Dolerite Dyke in Granite.

## (iii) Inclusions.

Throughout the dolerite small inclusions of quartz and felspar are visible. Quartz grains are very abundant, and a few measure up to half an inch across.

Fig. 2 shows two such xenocrysts, which measure 3.5 mm. The quartz is corroded, but there is no reaction at the border. The presence of liquid bubbles in the quartz

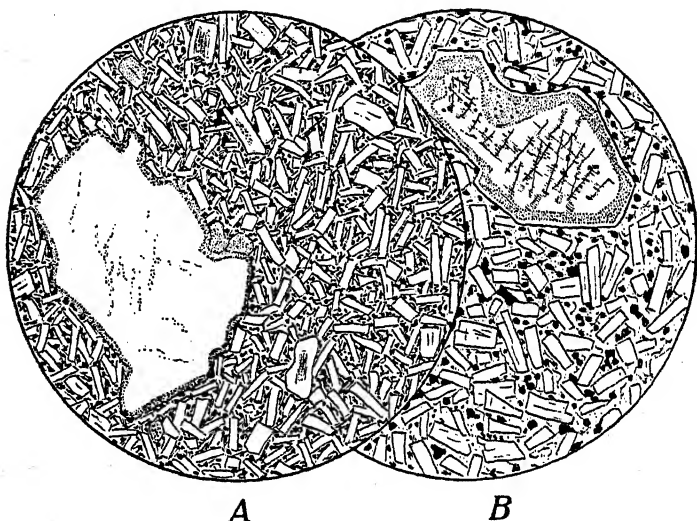


Fig. 2.

- A. Fine grained altered dolerite with corroded quartz xenocryst. The dolerite consists of albitized felspar, chlorite, carbonates and iron ore. The xenocryst is fringed with carbonates, but shows no reaction border.  $\times 10$ .
- B. Coarser grained dolerite with xenocryst of acid andesine. The dolerite contains an abundance of chlorite in the groundmass. The felspar xenocryst has a clear outer rim of albite, an altered zone consisting of sericite and chlorite, and the centre is partly albitized.  $\times 10$ .

suggests a plutonic origin. The felspar is zoned acid andesine, and there is no apparent high-temperature reaction, though slight alteration to chlorite, albite and sericite along a certain zone indicates that the deuteric solutions of the basic magma have altered the xenocrysts. The normal felspar in the dolerites is labradorite, often albitized, and that of the granite acid andesine.

## DISCUSSION.

It is obvious that the direction of the dyke is determined by the major jointing in the granite and the nature of the margins by the other joint directions. The two margins do not correspond, and this rules out the possibility of simple displacement (Billings<sup>(1)</sup>).

Stoping is suggested by the presence of the stringer of dolerite which, on the northern end of the dyke, penetrates along a joint-fissure and partly rifts off a mass of granite (see Fig. 1). It would appear that the magma was solidifying at this stage and had insufficient strength to rift off the granite block completely. Upstream the eastern contact again suggests this method of intrusion by short "side-stepping" from one joint-fissure to another. This evidence would suggest piecemeal stoping rather than the replacement of a large block.

The absence of the rifted blocks in the dolerite may be explained by supposing either that they sank in the fluid basaltic magma, or were removed to higher levels by an uprising current of magma (Billings<sup>(1)</sup>). The presence of deuterite minerals such as carbonates and chlorites in the dolerite suggests an abundance of low-temperature volatiles in the magma and a concomitant lowering of the temperature and viscosity. The removal of the blocks in such a magma would not be difficult.

The small fragments of quartz and felspar represent disintegrated fragments that have been mechanically shattered and distributed, the temperature being too low for assimilation.

The occurrence described is of interest because to the best of our knowledge it is the only recorded example of stoping in a small dyke. Obviously in a dyke of considerable width such as that of Medford, Mass., described by Billings<sup>(1)</sup>, replacement of the invaded rock must take place, but the emplacement of small dykes is generally attributed to lateral displacement of the wall-rock.

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## THE ELECTRODE POTENTIAL OF THIN FILMS OF ZINC ON PLATINUM.

By D. P. MELLOR, M.Sc.,  
and H. MULHALL, B.Sc.

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In view of the widespread application of protective metal films the electromotive behaviour of such films in their early stages of formation is of some interest. How many atomic layers of a metal such as zinc, for example, must be plated out on a polished platinum electrode before the electrode assumes the same potential with regard to a solution containing zinc ions as a massive zinc electrode? Several efforts have already been made to answer this question.\* Among the early attempts was that made in 1887 by Oberbeck (*Wied. Ann.*, 1887, 31, 336; see also Königsberger and Müller, *Phys. Zeitschr.*, 1905, 6, 847), who plated out various metals on platinum and then estimated the thickness of the metal film by applying Faraday's laws. Oberbeck found, for example, that on platinum a film of zinc  $2.54 \times 10^{-7}$  cm. thick was required to produce the potential of zinc. Nichols (*Journ. Am. Chem. Soc.*, 1935, 57, 267) suggested that as Oberbeck's method assumes, unjustifiably, a 100% current efficiency for the metal ion deposition, a better method would be to allow a cell  $\text{Pt}|\text{CuSO}_4|\text{Zn}$  to plate out the metal itself by short-circuiting the electrodes and then to determine the amount of the metal deposited by analytical methods. Using the cell  $\text{Pt}|\text{CuSO}_4|\text{Cu}$ , for which  $E = 0.281$ , v. Nichols obtained film thicknesses of the same order as Oberbeck's. In attempting to repeat Nichols' results it was found that the E.M.F. of the above cell was altered considerably (0.281 to 0.0280) by exclusion of air from the electrolyte

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\* With regard to the deposition of hydrogen ions on mercury and polished platinum cathodes, it has been shown that it takes considerably less than an atomic layer to establish electrode potential changes of 0.7 volt. (Bowden and Rideal, *Proc. Roy. Soc.*, 1928, 120, 63; Mellor and McAulay, *Nature* 1928, 122, 171.)

(copper voltameter solution).\* On account of the small initial E.M.F. of the cell used by Nichols it was decided to try the cell  $\text{Zn}|\text{ZnSO}_4|\text{Pt}$ , for which  $E=1.158$  v.

#### EXPERIMENTAL.

In his work on this cell Oberbeck used a neutral zinc sulphate solution prepared by boiling C.P. zinc sulphate with zinc carbonate for some time and then filtering. A similar solution was used in the present work. A sheet of polished platinum (apparent surface 39 cm.<sup>2</sup>) served as cathode. A wide-mouthed round-bottomed flask was used as a cell, and the electrodes were made to pass through glass tubing in a rubber stopper. A glass tap was also fitted to enable air to be pumped out from the cell. E.M.F.'s were measured with a Cambridge potentiometer, in conjunction with a galvanometer whose sensitivity was such that a current of  $5 \times 10^{-9}$  amps. produced a deflection of 1 mm. with the scale at a distance of 1 m. Small currents were thus unavoidably drawn from the cell under investigation, but measurements were made as rapidly and as infrequently as possible in all save the preliminary experiments with smaller sheets of platinum. More suitable null instruments such as the electrometer valve or quadrant electrometer were not available at the time. Zinc was estimated volumetrically with potassium ferrocyanide by using 1% diphenylamine in concentrated sulphuric acid as internal indicator. Titrations were carried out with a micro-burette and check runs were made on solutions containing zinc at a concentration of 1 mgm./cc. A cell was set up, and after the air had been removed was allowed to stand overnight. The initial E.M.F. was found to be 1.158 v. After being short-circuited for five days, the E.M.F. fell to 0.050 volts. The grey deposit of zinc which could easily be detected on the electrode was washed first with cold and then hot distilled water to remove all traces of zinc sulphate solution. The film was then removed from the platinum with hot dilute sulphuric acid.

#### RESULTS.

As a mean of three determinations, the amount of zinc deposited on the platinum was found to be 8.4 mgm.

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\* If Pt and Cu were short-circuited in  $\text{CuSO}_4$  solution to which neither sulphuric acid nor alcohol was added, a deposit of well crystallised cuprous oxide was formed on the platinum.

Assuming that the density of the zinc in the thin film is the same as that of massive zinc, that the film thickness is uniform, and that the accessible surface of the platinum is 2.1 times that of the apparent surface, one can show that amount of zinc corresponds to a film of uniform thickness  $1.45 \times 10^{-5}$  cm., a value considerably higher than Oberbeck's.

In order to see what effect the cell solutions might have on the result, a bath was made up, having the composition

|      |    |        |                    |
|------|----|--------|--------------------|
| ZnO  | .. | 88 gm. | } 200 cc. of water |
| NaCN | .. | 20 gm. |                    |
| NaOH | .. | 2 gm.  |                    |

A film of approximately one-tenth the thickness found with a zinc sulphate bath was obtained—a result which seems to indicate that the covering power and uniformity of film thickness depends on the nature of the cell solution. The potential of massive zinc in the complex cyanide solution is of course entirely different from its value in zinc sulphate solution. However, the criterion that the zinc film shall reach the same electrode potential as massive zinc still applies. Although hot dilute sulphuric acid (c. 4N) readily removed all detectable traces of zinc from platinum, the potential, in zinc sulphate solution, of a platinum electrode from which a zinc film had been just removed, was never quite the same as that of a clean polished platinum surface. This was due either to alloying of the zinc with the platinum or to the fact that a small proportion of zinc atoms was tenaciously held to the more active centres on the platinum cathode. Debye photographs\* of platinum wires short-circuited in the same way as the sheet platinum failed to reveal any evidence of alloy formation. This was not altogether surprising, since X-ray examination is not well adapted for testing this point. Furthermore, the alloy may have been removed by treatment with sulphuric acid. The alloying of zinc and platinum in electro-analyses has been frequently observed (see Quantitative Analysis by Electrolysis, Classen, 1913, p. 158, J. Wiley & Sons). Small amounts of platinum are removed from the electrode when the zinc deposit is dissolved in sulphuric acid. Another interesting phenomenon observed was the increase in E.M.F. of a once shorted cell to almost its original value on open circuit.

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\* We are indebted to Mr. S. Cohen for taking these powder photographs.

For example, a cell  $\text{Pt}|\text{N.ZnSO}_4|\text{Zn}$  which showed an original E.M.F. of 1.158 v. was short-circuited until the E.M.F. fell to 0.058 v. On standing on open circuit for some time the E.M.F. rose to 0.959 v. Nevertheless the platinum electrode was found to have a deposit of 8.4 mgm. of zinc on it. This behaviour on open circuit was observed several times and also with films of cadmium on platinum. When such films were viewed under a metallographic microscope isolated bright areas of platinum could be seen shining through the duller zinc or cadmium. No explanation for this behaviour on open circuit can be offered.

### DISCUSSION.

At the outset it may be stated that the film thickness of zinc ( $1.45 \times 10^{-5}$  cm.) observed on short-circuited platinum electrodes is not considered to have any special significance in regard to the question propounded at the beginning of this paper. There is evidence that the protective effect and electromotive behaviour of a very thin zinc film depends to some extent on the composition of the electrolyte from which the film is deposited and the rate at which the film is deposited. It is well known that crystal grain-size and orientation and other characteristics of an electrolytic deposit depend upon the physical and chemical conditions of deposition. Similar factors must affect the character of zinc films (on platinum) formed as a result of short-circuiting. The film thickness measured in these experiments is approximately one-hundredth of the thickness of zinc films used to protect iron against corrosion. It is much greater than that recorded by Oberbeck for zinc on platinum, a fact which may well be due to the very different rates at which the films were formed. With films formed during the course of four or five days, alloying may be more extensive, and the lack of uniformity of film thickness may be more marked owing to larger crystal grain size of the deposit. The growth of a film may commence at isolated spots on which quite thick deposits form, while the surrounding areas are still relatively thin. It is quite certain that films much thinner than  $1.4 \times 10^{-5}$  cm. may exert a protective effect, and presumably behave as the massive metal. In addition to Oberbeck's work there is modern experience with films of rhodium of the order  $2 \times 10^{-7}$  cm. thick which will protect silver against tarnishing (*Chem. Trade Journ.*, 1936, 99, 238). It seems, therefore, that the method of short-



circuiting devised by Nichols is not so well adapted for investigating thin metal films as direct plating out.

It seems doubtful whether it will be possible to answer definitely the question as to how many atomic layers of zinc must be placed out on platinum to produce the potential of a zinc electrode. This applies particularly to a polished platinum surface. In addition to the difficulty of being certain whether the films possess uniform thickness, there is the further difficulty of estimating the specific surface of the platinum. Where the fissures and projections of a surface are of molecular dimensions, it is clear that the accessible surface will depend on the dimensions of the atoms and molecules constituting the surface film. The value for the specific surface assumed in the calculation of film thickness of zinc was taken from Bowden and Rideal's paper (*Proc. Roy. Soc.*, 1928, 120, 63), and is really a measure of the accessibility of the platinum surface to hydrogen. The value 2.1 is admittedly a very rough approximation for calculation, but it represents at least the right order. If the specific surface is made to approach more closely the apparent surface by thorough polishing, the chances of alloy formation with the deposited metal are increased. The evidence on this point is particularly clear from the interesting work on electron diffraction of Finch, Quarrel and Roebuck (*Proc. Roy. Soc.*, 1934, 145A, 676) on the Beilby layer.\*

"In many cases the Beilby polish layer has the remarkable property, not shared by the corresponding crystalline surface, of dissolving crystalline metal films deposited thereon. Thus at room temperature zinc crystals dissolved rapidly on polished copper and somewhat less rapidly in polished mild steel surfaces, but are insoluble in either of these surfaces after the Beilby layer has been removed by etching. With sufficient deposition the Beilby layer becomes saturated, whereupon further deposited layers retain their crystal structure indefinitely. Similar effects have been observed with Zn, Sn, Pb and Ag flashed on to copper, mild steel, lead and gold surfaces; and with cadmium and Li films condensed on a copper polished layer. More recently we have found that whilst 30 seconds' electro-deposition at 0.1 amp/dm<sup>2</sup> sufficed to form a permanent crystalline zinc layer on crystalline copper,

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\* It is most probable that the Beilby layer on the platinum used in these experiments was destroyed after the first film was formed. Alloying seems to occur even with crystalline surfaces.

three minutes were necessary if polished copper served as a base metal." (*Trans. Far. Soc.*, 1935, 31, 1077.)

Assuming a 100% current efficiency of zinc deposition, and that the apparent and true surface of polished copper are identical, the latter deposit corresponds to a film thickness of approximately  $10^{-5}$  cm.—the same order as observed on the short-circuited platinum electrodes. This similarity of film thickness in the two cases is in all probability a mere coincidence. In a more recent paper (*Trans. Far. Soc.*, 1936, 32, 852), Finch and Sun again refer to this alloying of a film with the underlying substrate, stating that it is quite probably a general effect with electro-deposition on polished surfaces.

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## SOME OBSERVATIONS OF ZONAL DISCORDANCES IN DIURNAL MAGNETIC VARIATIONS.

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(With four text-figures.)

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When making magnetic surveys in connection with geophysical prospecting it is necessary to correct total recorded variations from station to station for the portion of the diurnal variation which has taken place during the time interval between readings. For a small scale survey, where distances concerned are not great, but where great precision is required, this can be done by checking back to a sub-station (established in the area), between every reading, so as to determine departures from an initial reading there; that is laborious and expensive from the point of view of time so that, in general practice, readings are taken on the sub-station at the commencement of the observations for the day, at about midday, and on closing the survey in the evening. Variations thus noted, partly instrumental and partly due to diurnal variations (other necessary corrections having been made), are then distributed as corrections over the stations. This presumes a uniform change in the magnetic components over a morning and afternoon period, which in general is quite justified.

Another method of correction is to obtain hourly readings from a fixed station; in the magnetic survey records of the United States of America,\* a sufficiently close relation exists between the diurnal magnetic variations over the whole range of continental longitudes, for wide bands of latitude, to justify a general statement that the major daily variations are zonal and not merely local. Accepting this, it has frequently been the practice in the eastern States of Australia to accept the readings of the magnetic

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\* See also Chapman, "The Earth's Magnetism" (Methuen, 1936), p. 36.

station of the Victorian Government (at Toolangi, Victoria) as giving the variations sufficiently accurately for the eastern zone, though the method of checking in regularly on a local base is always employed in addition.

Fixed magnetic stations, both in the United States and here, are chosen on areas of "magnetic flats", where the variation from point to point in the district is slight, and the ground to a considerable depth is of non-magnetic materials, the surface also being level. Magnetic surveys for geophysical prospecting are not usually carried out over such "flats"; so that a comparison of diurnal magnetic variations on an area of local magnetic anomalies and on a "magnetic flat" seemed desirable.

Sets of readings have been taken at the research station "Hills and Dales", Mittagong, New South Wales, for comparison with the concurrent readings at Toolangi, Victoria; the author is indebted to Professor J. M. Baldwin, M.A., D.Sc., F.Inst.P., and Mr. W. M. Holmes, M.A., B.Sc., A.Inst.P., for information supplied from the latter station. The "Toolangi" Magnetic Observatory, on level ground, with very small local magnetic anomalies, is at an altitude of 1,500 feet above sea-level, in longitude  $145^{\circ} 28' \text{ E.}$ , latitude  $37^{\circ} 32' \text{ S.}$  "Hills and Dales" is on a hillside, on the eastern side of "The Gib", an asymmetrical laccolith of syenite, the ground in the vicinity of the station being crossed in one section by a basalt flow. It is 2,555 feet above sea-level, in longitude  $150^{\circ} 26' \text{ E.}$ , latitude  $34^{\circ} 28' \text{ S.}$  The nature of the country, physiographic and magnetic, is dealt with in an earlier paper.\* The Gib forms a hill rising 800 feet above the surrounding country, so that the station is both in the close proximity to a magnetic mass and is on a prominence. Advantage was taken of the basalt *in situ* to obtain sets of readings both on a local magnetic "high", and on a magnetic "low" zone in the immediate vicinity, the change being about  $750\gamma$  in 100 feet distance. The instrument employed at Mittagong was a vertical field balance of the Adolf Schmidt type, constructed by Askania-Werke Coy. The instrument is No. 88057, sensitivity  $40\gamma$  per division. The temperature correction was  $10\gamma$  per centigrade degree. Readings, necessarily, were not continuous, the instrument being in position on the sub-

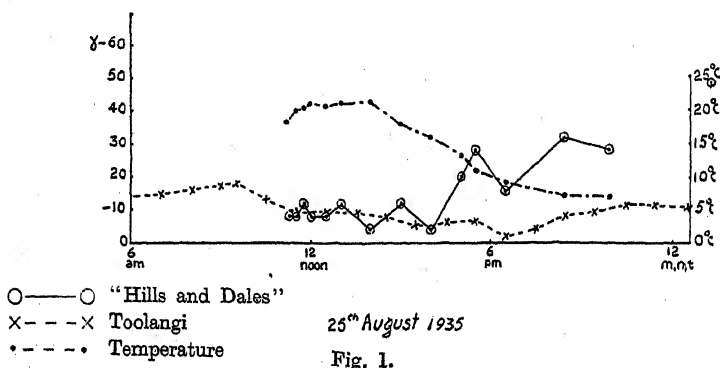
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\* Booth, E. H., "A Detailed Regional Magnetic Survey as an aid to Geological Interpretation", *THIS JOURNAL*, 1935, 69, 35.

station throughout the days of observation, and being put on and off suspension for each reading (usually hourly). Observations should be correct to 5γ.

The results, after full correction, show that though there is generally fair co-ordination with Toolangi readings, variations are far from concordant, and regularly show wide variations. This is illustrated by the diagrams accompanying the article.

Fig. 1 is a comparison of readings at Toolangi and at Mittagong on the 25th August; the instrument at Mittagong was in a position off the basalt, in what is a magnetic "low" for the area (in a pocket between two



basalt flows). The diurnal variation curves correspond throughout the day until after 4 p.m. (Eastern Standard Time, Australia),\* when there is a sharp drop in the vertical component at Mittagong, whilst that at Toolangi continues to rise; a discrepancy of the order 20γ continued through the evening.

Fig. 2 shows the record for the following day; in accord again at 6 a.m., the readings at both stations decrease, but there is a reversal at Mittagong three hours before it occurs at Toolangi, and the forenoon variation is also much greater at the former station than at the latter. Temperature curves, the temperatures being those recorded in the variometer, are given for Mittagong in each case; the magnetic curves have been corrected for the temperature changes.

\* Eastern Standard Time, Australia, is universal time plus ten hours.

As the variometer is open to suspicion on account of the fact that it is subjected to temperature changes (apart from any question as to error in the correction factor), whilst the observations at Toolangi are made at nearly constant temperature, Fig. 3 is included to give a day on which the temperature was constant in the instrument

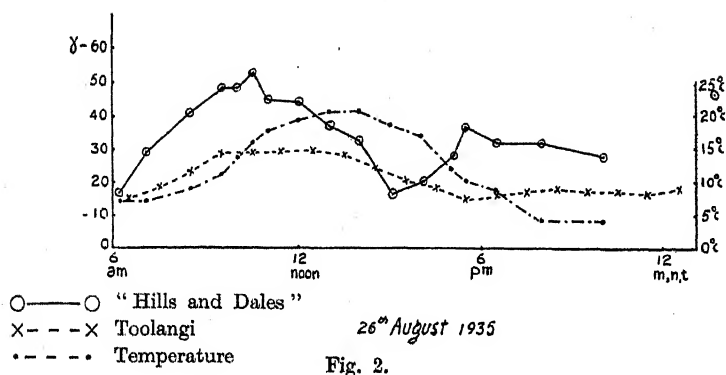


Fig. 2.

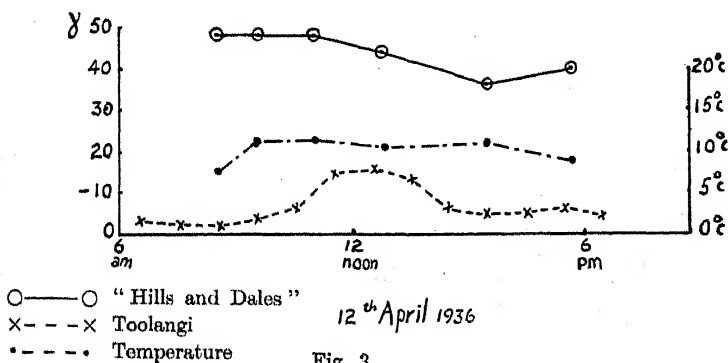


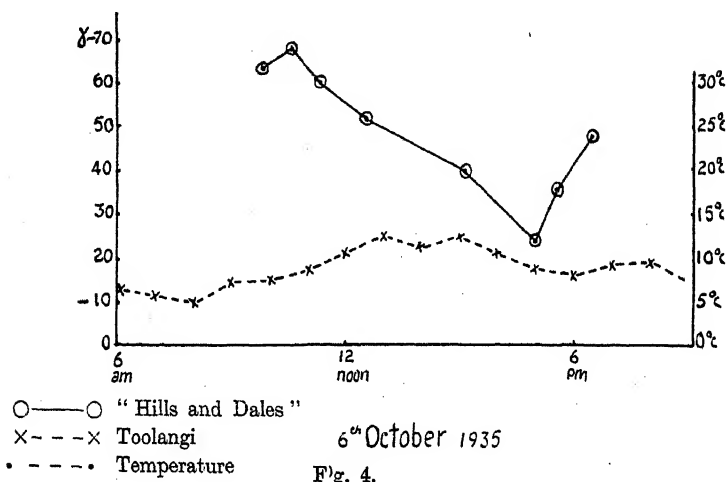
Fig. 3.

over a period of about seven hours. This is from the same sub-station as Figs. 1 and 2, and shows the departure from similarity of the curves even when no change in temperature correction was made; the readings were taken on 12th April, 1936, when the conditions at Mittagong were cloud, mist, no wind.

An example on the basalt, 100 feet from the previous sub-station, is given in Fig. 4 (as variations are being

compared, and the departures are shown relative to an arbitrary base line, the ordinates of the graph may be altered by the addition or subtraction of a constant, in any curve.)

Before proceeding to a discussion of the possible causes of these discrepancies, clearly not solely due to latitude differences, it is desirable to obtain continuous readings at Mittagong with two variometers, one of which is on a magnetic flat, whilst the other is at "Hills and Dales";



and to obtain continuous readings at "Hills and Dales" with a magnetograph in a constant temperature hut. The conclusion may be drawn from these observations made to date that it is not safe to accept the variations at an established magnetic station to apply as corrections to a survey over magnetic prominences, even on what may be magnetic "quiet-days", when the stations are so far removed from one another and not in the same latitude, though the longitudes may be approximately the same.

Acknowledgments are made to the Council of Scientific and Industrial Research and to the Australian and New Zealand Association for the Advancement of Science for placing at the use of the author the vertical field balance owned by those two bodies.

SOME OBSERVATIONS ON THE OCCURRENCE OF  
BILE PIGMENT HÆMOCHROMOGENS IN NATURE  
AND ON THEIR FORMATION FROM HÆMATIN  
AND HÆMOGLOBIN.

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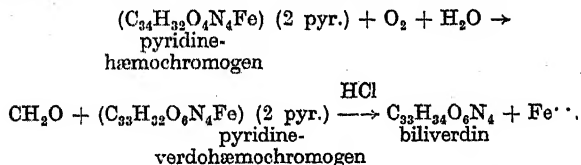
(The Charles Kolling Laboratory of the Institute for Medical Research,  
Royal North Shore Hospital, Sydney.)

(With one text figure.)

(Manuscript received, October 20, 1936 Read, November 4, 1936.)

Until quite recently there was no indication whatever of the way in which the formation of bile pigment from hæmoglobin takes place in the body, nor had bile pigment been prepared from blood pigment *in vitro*. Occasionally such a conversion has been claimed, but then there has been no clear evidence of the bile pigment nature of the substance obtained, which never had been isolated in a pure state. Often, moreover, the conversion had been carried out in a medium containing living cells; it is misleading to term "*in vitro*" reactions which occur in presence of tissue cultures or in total blood at 37°, as has been done.

Lemberg (1935) recognised the "green hæmin" of Warburg and Negelein (1930) as hæmochromogen of a bile pigment and transformed it into biliverdin. The latter substance had been obtained by oxidation of bilirubin with ferric chloride (Lemberg, 1932, 1934), and previously found in bird's egg shells ("oocyan", Lemberg, 1931) and in the dog's placenta ("uteroverdin", Lemberg and Barcroft, 1932). The reactions by which hæmin is transformed to biliverdin can be represented briefly as follows:

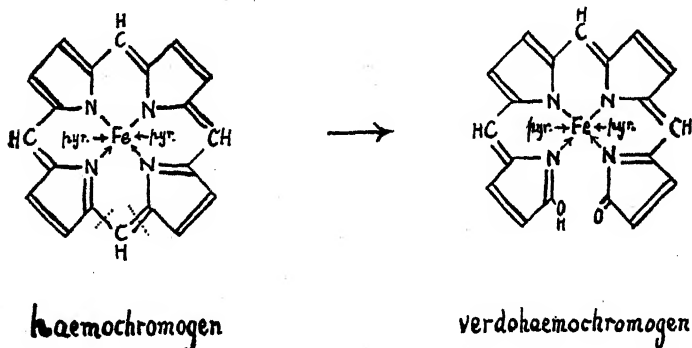



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\* Working under the T. E. Rofe Foundation.



and the following formulæ indicate the essential transformation of the hæmochromogen into the verdohæmochromogen. (The side chains have been omitted, since they remain unaltered; the two pyridine molecules are situated above and below the plane formed by the iron atom and the tetrapyrrolic substance):



The formula of verdohæmochromogen as a bile pigment hæmochromogen with an open tetrapyrrolic chain (but kept together in ring form by the central iron atom) was proved by its easy transformation into known bile pigments by reduction, action of acids and oxidation. In the two first mentioned cases this is accompanied by the loss of iron, which is rendered much more easily detachable by the opening of the ring. Some additional evidence of the bile pigment nature of verdohæmochromogen will be brought forward in this paper.

The suggestion has been made by Lemberg (1935) that the breakdown of hæmoglobin to bilirubin in the body proceeds in a similar way, a verdohæmochromogen and biliverdin being intermediate steps.

This hypothesis has been supported by the work of Lemberg and Wyndham (1936), who showed that biliverdin is reduced to bilirubin in the liver and in other tissues by dehydrogenase systems.

In this connection one paper should be mentioned which escaped our notice in the previous publication. Kanasaki (1933) observed that the green bile found in the duodenum of a case of liver cirrhosis became rapidly yellow after intravenous injection of hypertonic glucose solution. The presence of biliverdin in human bile in cases of liver damage has been observed repeatedly. Kanasaki ascribes

it to the action of oxidases, but it is better explained by the depletion of the glycogen store in the diseased liver, glycogen being the substrate for the enzyme systems causing the reduction of biliverdin. We have recently reported that lactic acid, the product of glycolytic breakdown, is one of the most active hydrogen donors for the reduction of biliverdin to bilirubin. By injection of hypertonic glucose solution glycogen is forced upon the liver, and hence biliverdin becomes reduced. The observation of the colour of duodenal contents is probably a means of recognising a low glycogen store in the liver.

In the present paper we are going to show that verdohæmochromogens and related compounds actually occur in cells, although in small concentration, and that they are easily formed in processes which are likely to occur in living cells. We shall also report some preliminary experiments on the removal of iron from verdohæmochromogens.

#### EXPERIMENTAL.

##### Occurrence of Verdohæmochromogen in Horse Liver Catalase.

Stern (1936) prepared concentrated solutions of horse liver catalase and subjected these to the action of acetone and hydrochloric acid in order to isolate the hæmin contained in this enzyme. As a by-product he obtained a blue-green pigment, which he was kind enough to transmit to one of us (R.L.) for investigation. The properties of the substance proved beyond doubt that it was biliverdin. From acetic acid-acetate buffer it was extracted by ether with blue colour; 1% hydrochloric acid extracted it again with green colour from the ether solution. It gave the typical red fluorescence reaction with zinc acetate and iodine, and the biliviolin-zinc compound thus obtained showed an absorption band with its centre at 635 m $\mu$ .

The way in which biliverdin had here been obtained by Stern from horse liver suggested that, previous to the treatment with acetone-HCl, biliverdin had been present combined with a protein (as hæmin is combined with a protein in catalase). There was, however, no evidence that iron had been a part of the molecule, as it is in verdohæmochromogen. Stern mentions his catalase solutions as showing absorption in the far red, which can be either ascribed to biliverdin or to oxidised verdohæmochromogen.

Reduced verdohæmochromogen, however, has a distinct absorption band between 660 and 650  $m\mu$ , for which we have now searched. We have indeed found this band in strong solutions of catalase, after addition of alkali, pyridine and hyposulphite.

For the preparation of catalase we have followed the methods described by Zeile (1930) and Stern (1936). The solutions thus obtained had a  $k$  (monomolecular reaction constant of  $H_2O_2$ -decomposition at  $0^\circ C.$ ) of 10–60,000 and a catalase factor ( $k : g$  substance in 50 c.c. enzyme solution) of 20–50,000. In one case we obtained a  $k$  of 500,000 and a catalase factor of 385,000, but we have, so far, been unable to reach similar values.

The dark brown solution showed the enzyme spectrum described by Zeile in thin layers. On reduction with sodium hyposulphite in presence of 1% potassium hydroxide and pyridine the solution at once gave the following spectrum (centre of the bands measured with the Hartridge Reversion Spectroscope): I, 651.8; II, 558.9; III, 524.0 (stronger part 528.7); IV, 498.1  $m\mu$ . Intensities: II, III, I, IV (weak).

This spectrum is clearly that of a mixture of protohæmochromogen (derived from the catalase) with a smaller amount of verdohæmochromogen, the bands II and part of III belonging to protohæmochromogen, the bands I, part of III, and IV to verdohæmochromogen. From this spectrum and the finding of biliverdin after treatment with acetone-HCl it can be safely concluded that the substance is a protoverdohæmochromogen. In the earlier publication the absorption bands of pyridine-verdohæmochromogen had been observed at 662, 533 and 501  $m\mu$ . The correct situation of the first band is somewhat difficult to establish, since oxidation shifts the absorption towards the infra-red, while hyposulphite in excess causes alteration with a shift towards the violet. Recent observations have shown us that the correct situation is probably between 650 and 655  $m\mu$ . In comparing it with the verdohæmochromogen of catalase one has to remember that the nitrogenous component of the green pigment in catalase is a protein compound and not pyridine, a fact which might cause a difference in the situation of the bands.

#### Occurrence of Bile Pigment Hæmochromogens in Cytochrome.

Bigwood *et al.* (1933, 1934) have observed the existence of an absorption band in the red part of the spectrum in

solutions of cytochrome c prepared from baker's yeast by the method of Hill and Keilin (1930). We can confirm this observation and show that this substance is a verdohæmochromogen.

Cytochrome c was prepared from 1 kg. of fresh baker's yeast (Cyco-yeast, Compressed Yeast Co., Sydney). The fresh sulphite-hyposulphite extract of the pre-extracted yeast showed a weaker, but quite distinct band at  $654.5 \text{ m}\mu$  in addition to the typical bands of cytochrome c [ $550.8$  (sharp) and  $521.8$  (less distinct and threefold)]. A separation of the substance causing the absorption in the red from cytochrome became possible by a fractional precipitation with  $\text{SO}_2$ .

When the first fine precipitate appeared, the solution was several times sucked through a hardened filter on a Buchner funnel. The  $\text{SO}_2$  precipitation was repeated once more, the second precipitation filtered off in the same way, and the remainder of the cytochrome precipitated by introducing more  $\text{SO}_2$ , shaking with air and allowing to stand. When the third precipitate was dissolved in a small amount of alkali and reduced by hyposulphite, it displayed the spectrum of cytochrome c free from the absorption in the red. The substance causing this absorption was contained in the earlier precipitates, in the first almost free from cytochrome c, in the second mixed with about equal parts of cytochrome c. The absorption spectrum of the first fraction was I,  $651.7$ ; II,  $550.2$ ; III,  $531.1$ ; IV,  $499.8 \text{ m}\mu$ . Intensities: I, III, II, IV. The weak band II is caused by cytochrome c, whereas I, III and IV clearly indicate the presence of a verdohæmochromogen. We have regularly observed the absorption band in the red in the fresh extracts, even if the access of atmospheric oxygen during the standing with sulphite-hyposulphite and during the filtration through kieselguhr was avoided as much as possible; we have, however, so far not been able to repeat the separation from cytochrome c owing to the difficulty of obtaining a filterable precipitate.

When the solution of the first fraction, containing the verdohæmochromogen, was left standing in contact with air for one day, an alteration of the spectrum (after reduction) was observed. The strong absorption band was now found shifted towards the blue end of the spectrum (to  $634 \text{ m}\mu$ ). A similar change is observed when verdohæmochromogens undergo autoxidation (Lemberg, 1935).

This process consists in the dehydrogenation of verdo-hæmochromogen (an isobiliverdin-iron complex) to a biliviolin-iron complex containing two atoms of hydrogen less than the former. Biliviols are bile pigments of red-violet colour in neutral, blue-violet to violet colour in acid solution which possess very typical properties; for example, the formation of zinc complex salts with a strong red fluorescence and two absorption bands (a strong one between 622 and 637  $m\mu$  and a weaker one between 575 and 585  $m\mu$  (cf. Lemberg, 1934). In an investigation which will be published separately, we have established that there is a variety of different isomeric biliviols (and mesobiliviols), at least three of each, which are difficult to distinguish from one another, and which differ only in the situations of the double bonds in the molecule. It is to be borne in mind that "biliviolin" and "mesobiliviolin" are used here as collective terms, and are not terms to be ascribed to definite compounds. The biliviols form hæmochromogens with pyridine, hyposulphite and ferrous salt in ammoniacal solution, which possess an absorption very similar to that of the zinc compounds mentioned above, but do not fluoresce.

An absorption band in the red cannot be seen in the yeast itself, so that the verdo-hæmochromogen is probably formed from a precursor during the extraction of the yeast with sulphite-hyposulphite. This precursor might be cytochrome a, which disappears during the extraction process.

Bands in the region of 630  $m\mu$ , however, have been described in the cytochrome spectrum of several bacteria (Azotobacter, Acetobacter, *B. coli*, and pathogenic intestinal bacteria) as cytochrome  $a_2$  [Negelein and Gorischer (1934), Keilin (1934), Fujita and Kodama (1934)]. Like the band of cytochrome  $a_2$ , the absorption band of the biliviolin-hæmochromogens is shifted towards the infra-red by oxidation, and is immediately destroyed by ammonium sulphide. These facts make it probable that cytochrome  $a_2$  is a biliviolin-hæmochromogen. Warburg and his collaborators who found this band at first in bacteria with high respiratory activity and observed alterations of the band with  $O_2$  and CO, believed it to be the spectrum of the respiratory ferment of these bacteria, but from the work of Keilin and the Japanese authors it is more likely that the compound belongs to the cytochrome complex. From the fact that cytochrome a is missing in those bacteria in

which cytochrome  $a_2$  is observed, Keilin concluded that  $a_2$  is derived from  $a$ . If our assumption of the bile pigment hæmochromogen nature of cytochrome  $a_2$  is correct, its formation from cytochrome  $a$  within the bacterial cell would be similar to that reaction which causes the presence of verdohæmochromogen in cytochrome  $c$ , although the latter process probably occurs *in vitro*.

#### Bile Pigment Hæmochromogen in Blood Extracts.

We have also observed the formation of verdohæmochromogen from a precursor in a hæmoglobin-free extract prepared from horse erythrocytes by the method of Tsuchihashi-Zeile (Zeile, 1930).

The cells of one litre horse blood were centrifuged off, washed twice with isotonic saline and hæmolyzed with water and some ether. An equal volume of alcohol was added and hæmoglobin removed with chloroform. From the aqueous layer the pigment was absorbed to aluminium hydroxide [prepared according to the method of Willstätter and Racke (1921)] and eluted by  $m/10$  secondary phosphate solution.

The greenish-yellow solution contained catalase, the spectrum of which was visible in a layer 40 cm. long. After reduction with hyposulphite in presence of alkali and pyridine the protohæmochromogen spectrum was visible in a layer of 14 cm. and in addition to this a weak but sharp band at about 580  $m\mu$  (measured with the hand-spectroscope). In two minutes, however, these bands were replaced by the following spectrum (measured in the Hartridge Reversion Spectroscope in 15 cm. layer): 655 (distinct), 574.3 (very weak), 529.0 (strong), 499.6  $m\mu$  (very weak). The first and the third band make the presence of verdohæmochromogen probable, although the strength of the third band indicates the presence of additional compounds. Under the condition of the experiment and during the same time neither protohæmochromogen nor catalase, cytochrome  $c$ , "hæmochromogen  $c$ " (Roche) gave rise to verdohæmochromogen. Since both the band at 580  $m\mu$  and the bands of protohæmochromogen disappear and are replaced by those of verdohæmochromogen, it is perhaps the interaction of both hæmochromogens that causes the rapid production of verdohæmochromogen in this extract. Additional evidence for this is, however, required.

In extracts from pig's erythrocytes we have not observed the same phenomenon. The hæmoglobin-free extract showed absorption bands at 567.0 and 539.0  $m\mu$  (the last mentioned stronger). Reduction with hyposulphite caused the appearance of an additional band at 626  $m\mu$ . After addition of pyridine a strong protohæmochromogen spectrum appeared with additional weak bands in the red and orange. A weak band in the red was also found in the hæmochromogen obtained from pig's serum. It should be noted that the spectroscopic examination was always carried out a few seconds after addition of the reducer, so that no secondary alterations are likely to have taken place, nor is such an alteration likely to occur during the process of hæmoglobin removal. The observations indicate the presence of small amounts of verdohæmatin in pig's erythrocytes and serum.

**Action of Atmospheric Oxygen on Different Hæmochromogens and on Hæmoglobin in Presence of Reducing Agents.**

An extensive study is being made of the autoxidation of hæmochromogens and hæmoglobin in presence of reducing substances. While this study is only in its early stages, it has already shown that both types of hæmochromogens, those with the strongest absorption band near 655 $m\mu$  and those with the band near 630  $m\mu$ , are produced under very similar circumstances, and that the last mentioned probably arise by a further oxidation of the former (verdohæmochromogen).

Table I gives a number of results of such experiments in which various hæmochromogen solutions in weak alkali or neutral hæmoglobin solutions were exposed to atmospheric oxygen.

Pyridine-hæmochromogen is the compound most easily converted into verdohæmochromogen. The experiments of Fischer and Lindner (1926), of Warburg and Negelein (1930), and of Karrer, v. Euler and Hellström (1933) have already shown that a variety of reducing agents can serve for this purpose. The most striking action is that of ascorbic acid (Karrer and co-workers) and this substance is probably—at least partly—responsible for the same action of tissue and yeast extracts (Fischer and Lindner) which these authors found to be due to a heat-stable principle. We have identified the product of all these reactions with verdohæmochromogen by means of its spectrum, and in several cases by transformation into

TABLE I.

| Type of hæm compound.                | Reducing substance.          | Absorption band after addition of pyridine and $\text{Na}_2\text{S}_2\text{O}_4$ in $\mu\text{u}$ . | Remarks.  |
|--------------------------------------|------------------------------|---|---|
| Protohæm + egg albumen               | Hyposulphite.                | 628   |   |
| Protohæm + glycine ..                | Hyposulphite.                | 628   |   |
| Pyridine — protohæmo-chromogen .. .. | Great variety of reductants. | 655   | Rapidly with ascorbic acid, identified as <i>verdo hæmo-chromogen</i> in several cases. |
| Ammonia — protohæmo-chromogen .. ..  | Hyposulphite, ascorbic acid. | 627   |   |
| Protohæm + tryptophane               | Hyposulphite.                | 628 and 655   |   |
| Protohæm + tryptophane               | Ascorbic acid.               | 655   | Strong.   |
| Globin — protohæmo-chromogen.        | Ascorbic acid.               | 655   | Slowly.   |
| Adrenaline — protohæmo-chromogen.    | Hyposulphite.                | 630   |   |
| Globin — "hæmo-chromogen c" ..       | Hyposulphite.                | 659<br>628·3  | After first reoxidation. After repeated reduction and oxidation.                        |
| Pyridine — "hæmo-chromogen c" ..     | Hyposulphite.                | 634·0   | Identified as biliverdin-iron salt by splitting with $\text{HCl}$ .                     |
| Hæmoglobin .. ..                     | Ascorbic acid.               | 630·1   |   |
| Hæmoglobin .. ..                     | Cysteine.                    | 630<br>655  | In solution. In alkaline solution of green precipitate.                                 |
| Hæmoglobin .. ..                     | Adrenaline.                  | 630·1   |   |

biliverdin. Protohæm + tryptophane is converted by ascorbic acid much more readily to verdohæmochromogen than globin-hæmochromogen. With hyposulphite it also gave the hæmochromogen with the 630  $\mu\text{u}$  band, and the latter alone was obtained from ammonia-hæmochromogen, adrenaline-hæmochromogen\* and from hæm in presence of egg albumin and glycine.

\* Adrenaline hæmochromogens possess remarkable properties which will be described in detail elsewhere. Their bands differ considerably from those of other hæmochromogens, and this difference is still increased by addition of pyridine or denatured globin in small amounts, whereas large amounts of pyridine displace adrenaline.



In this connection it is important to mention that verdohæm unites with native globin, but that the compound obtained is not verdohæmoglobin, but verdohæmochromogen, since it does not unite reversibly with oxygen, but is oxidised by it to a ferri-hæmochromogen\* (parahæmatin) compound. Under the same conditions hæm gave hæmoglobin. Only the "hæmatin c" of Roche and Bénévent (1935) behaves like verdohæmatin. Hæmatin c is the name given by Roche and Bénévent to a substance which is obtained by repeated alternate reduction (by hyposulphite) and oxidation (by ferricyanide) of pyridine-hæmochromogen. The spectrum of hæmochromogen c had previously been observed by Keilin; it is very similar to that of cytochrome c; we do not, however, agree with Roche, who believes that the structures of the two compounds are also similar. This assumption, which was first made by Keilin, has been disproved by Zeile (1932). We have repeated the experiments of Zeile and can confirm them. They show that the transformation of hæmatin to hæmatin c is of a complex nature, that sulphur enters the molecule, and that the reaction is independent of the presence of unsaturated side chains, mesohæmatin also giving rise to a mesohæmatin c. The hæmatin of cytochrome c, however, differs from protohæmatin in the side chains only, and can be converted into hæmatoporphyrin. We also do not agree with Roche when he concludes from his experiments that the globin in hæmoglobin is bound to the unsaturated side chains of protohæm. The existence of a mesohæmoglobin (Hill) and our observations that mesoverdohæmatin and mesohæmatin c behave exactly like the corresponding compounds with vinyl side chains prove that the side chains are irrelevant for hæmoglobin formation, and that not altered side chains but the altered nucleus causes the abnormal behaviour of verdohæmatins and hæmatins c towards the globin.

The experiments with hæmatin c are mentioned here only for the reason that in this case the reaction of the globin-hæmochromogen with hyposulphite was particularly instructive. A verdohæmochromogen was obtained by the first oxidation by shaking with air, which by repeated reduction with hyposulphite and reoxidation was trans-

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\* Name suggested by L. Pauling and co-workers for the compounds of hæmatins with nitrogenous bases.

formed into a biliviolin-hæmochromogen. In this case the amount of the latter substance was sufficient to allow the preparation of biliviolin from it by splitting off the iron with hydrochloric acid, and identification of the biliviolin by its properties, particularly the characteristic zinc complex salt (absorption band at 637 m $\mu$  and red fluorescence).

In a separate paper experiments on the mechanism of the reaction by which verdohæmochromogen is obtained from hæmatin will be described. It can be shown that this is not a catalytic action of the hæm iron in the sense that the hæm iron oscillates between the ferric and ferrous states. A mixture of hæmatin and hæmochromogen can be kept in nitrogen for long periods without any verdohæmochromogen being formed, and the verdohæmochromogen formation is not inhibited by cyanide. The oxidation is also not due to the action of hydrogen peroxide, which might be assumed to be formed at first by a by-reaction and then cause the oxidative splitting of the porphyrin nucleus. Hæmochromogen, ascorbic acid and dilute hydrogen peroxide (or various other peroxides) do not react in absence of oxygen, whereas in its presence verdohæmochromogen is rapidly formed under conditions otherwise the same. The reaction is thus to be considered as a true autoxidation of hæmochromogen.

Hæmoglobin in the presence of a great variety of reducing substances is transformed by oxygen into an insoluble "green pigment" [Anderson and Hart (1934)], which is also produced by the action of pneumococci and streptococci on hæmoglobin. It consists of a complex mixture of hæmatin and various oxidation products. As Table I shows, it also contains small amounts of biliviolin-hæmatin (and occasionally verdohæmatin).

#### Transformation of Verdohæmochromogen into Biliverdin.

Fischer and Halbach (1936) have recently mentioned the observation that the reduction of verdohæmochromogen with hydriodic acid in acetic acid yields traces only of bilirubic acid, whereas this compound is obtained in good yield from bilirubin. Since Fischer has not said whether or not he regards this observation as evidence against the bile pigment nature of verdohæmochromogen, it is necessary to point out that it cannot be regarded as such evidence. Biliverdins, unlike bilirubin, do not readily give rise to bilirubic acid, since the splitting of bilirubin into the

dipyrromethanes depends on the presence of a  $\text{CH}_2$  group in the centre of the bilirubin molecule which is not present in the biliverdins. The iron of verdohæmochromogen, moreover, is so easily removed by mineral acids that biliverdin must arise by the treatment with hydriodic acid before the splitting processes occur. The iron from globin-verdohæmochromogen, for example, is liberated by the action of various agents to the following extents: by precipitation with trichloroacetic acid, 35%; by pyrophosphate and following precipitation with trichloroacetic acid, 57%; by standing twenty-four hours at  $37^\circ$  with N/10 hydrochloric acid, 62%; by boiling for a few seconds with 5N HCl or by boiling for three minutes in 1% HCl, 90%. That the pigment obtained by acid from verdohæmochromogen is biliverdin, has been shown by Lemberg (1935). We have also obtained biliverdin by action of hydrazine hydrate and glacial acetic acid on verdohæmochromogen.

#### DISCUSSION.

The facts brought forward in this paper support the hypothesis that verdohæmochromogens are intermediate products of bile pigment formation in the body.

The presence in the horse liver of a verdohæmochromogen with a protein as nitrogenous constituent has been demonstrated. The concentration of this compound in the liver is small, but so is the concentration of bile pigment in this organ, although it is the main site of bile pigment formation. The way of separation of this verdohæmochromogen from hæmoglobin indicates that its protein component is not globin, but a protein similar to that present in catalase. If the total verdohæmochromogen of the liver is of this kind, the transformation of the globin of hæmoglobin into this protein would have to be considered as the first step in blood pigment katabolism. This is, however, not yet certain, since it may be that another part of the verdohæmochromogen of the liver, being globin-verdohæmochromogen, was removed together with the hæmoglobin, and thus escaped notice. Whether this is so can be decided only by further experiments, but the possibility must be kept in mind.

The detection of a small amount of verdohæmochromogen in pig's serum is of importance, since no bile pigment has yet been found in the blood of this animal, although there must be a way in which bile pigment is transported from

other sites of its formation to the liver. This transport form in the pig's blood is probably verdohæmochromogen. The occurrence of traces of verdohæmochromogen in the erythrocytes might open a new aspect, because it makes it probable that at least a small part of the bile pigment formation occurs in the erythrocytes themselves. We have also observed small amounts of verdohæmochromogen in extracts of horse erythrocytes, but they appeared to be of secondary occurrence. For this reason we do not yet consider our results as definite evidence for the actual occurrence of verdohæmochromogens in blood cells, since the amounts were very small and hence a secondary formation *in vitro* not altogether excluded. On the other hand globin-verdohæmochromogen, if present in the cells, would certainly be precipitated with the great excess of hæmoglobin, and even a verdohæmochromogen of the kind found in liver extracts might be lost to a great extent in the process of hæmoglobin precipitation from hæmolysed red cells.

The verdohæmatin-iron is easily detached. Compounds like pyrophosphate which form complexes with iron, are able to split off the iron, and, since pyrophosphate is a normal cell constituent, it might account for the ultimate removal of the hæm iron. If verdohæmatin compounds occur in the blood, they would be the source of a certain part of the "easily splittable" non-hæmoglobin iron (Barkan), as they certainly are in the liver; and, on the other hand, the study of the "easily splittable iron" might provide a method for establishing the existence of bile pigment hæmochromogens, where other methods fail.

#### SUMMARY.

Observations are dealt with on the formation of bile pigment hæmochromogens by autoxidation of hæmochromogens in presence of reducing substances and on their occurrence in nature.

The presence of verdohæmochromogens (iron complex salts of isobiliverdin) is established in catalase preparations from horse liver and in preparations of cytochrome c from yeast. The bearing of the first mentioned observation on the hypothesis that verdohæmochromogens are intermediate products of bile pigment formation in the animal body is discussed. Traces of verdohæmochromogens are found in hæmoglobin-free extracts from erythrocytes and serum of the pig.

On further oxidation verdohæmochromogens can be transformed into iron complex salts of biliviols. Evidence is brought forward to support the view that cytochrome  $a_2$  is such a biliviolin-hæmochromogen.\*

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\* The laborious preparations have been largely carried out by Mr. M. Norrie.

## ON THE CHEMISTRY OF JAFFE'S REACTION FOR CREATININE.

By ADOLPH BOLLIGER, Ph.D.\*

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*(Manuscript received, October 23, 1936. Read, November 4, 1936.)*

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Recently it has been shown that creatinine forms markedly coloured solutions, not only with picric acid in the so-called Jaffe's reaction (*Ztschr. f. physiol. Chem.*, 1886, 10, 391), but also with dinitro-benzoic acid (Bolliger, *THIS JOURNAL*, 1936, 69, 224; Benedict and Behre, *Jour. Biol. Chem.*, 1936, 114, 515), trinitro-benzoic acid, and trinitro-benzol (Bolliger, *THIS JOURNAL*, 1936, 70, 211). The compounds underlying these colour reactions have been considered to be molecular compounds according to the theory of P. Pfeiffer (*Chem. Zeitg.*, 1935, 69, 205). The mechanism of their formation was assumed to be as follows: On the addition of alkali creatinine becomes enolised and therefore attains aromatic properties, which makes it capable of forming deeply coloured molecular compounds with picric acid and certain other aromatic nitro-compounds. In order to prove this assumption, an attempt was made to isolate these molecular compounds and, if possible, to demonstrate their constitution.

In the first place the original Jaffe reaction, discovered in 1886 (*Ztschr. f. Physiol. Chem.*, 10, 391), i.e., the interaction of creatinine and picric acid in an alkaline medium, was studied. This reaction remained completely unexplained for a long time. In 1924 Greenwald and Gross (*Journ. Biol. Chem.*, 69, 601) expressed the opinion that a red tautomer of creatinine picrate is responsible for the red colouration observed in Jaffe's reaction. This red tautomer was obtained by acidifying with concentrated hydrochloric acid a concentrated mixture of creatinine, excess of sodium picrate, and slight excess of sodium hydroxide. This explanation of Greenwald does not appear to be quite satisfactory, because this isomeric compound is formed only in acid solution, while Jaffe's reaction

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\* Acknowledgments are due to Miss Dorothy Dark for valuable technical assistance.

succeeds only in an alkaline medium.\* In 1928 Greenwald described another compound of orange-red colour which was obtained by the addition of alcohol to a mixture of creatinine, sodium picrate, and sodium hydroxide (*Journ. Biol. Chem.*, 1928, 77, 539). This substance was not considered to be the true cause of Jaffe's reaction, because its watery solution is not deep enough to account for the red colour obtained in this reaction. This orange-red substance was found to consist of approximately two molecules of creatinine, one of picric acid, and three of sodium hydroxide. W. Weise and C. Trott (*Ztschr. f. Physiol. Chem.*, 1928, 178, 125) stated that the reaction between creatinine and picric acid is a special case of a reaction common to all compounds with an activated methylene group, and they considered it as a condensation process, on purely theoretical grounds.

In the course of the present investigation it was found that on mixing creatinine, picric acid, and alkali in an alcoholic medium, red crystalline substances are readily obtained. It was soon observed, however, that the composition of these substances depends to a certain extent on whether or not a substantial excess of picric acid or alkali, or both, is present. These substances all contain creatinine, picric acid, and alkali. They are readily soluble in water with deep red colour. In the present communication one of these substances will be specially dealt with.

#### EXPERIMENTAL.

##### The Preparation of Compound 1.

An approximately normal solution of alcoholic sodium hydroxide is prepared by dissolving pure sodium hydroxide in 99% alcohol. In about five c.c. of this solution are dissolved two millimols of creatinine (0.226 gm.). Creatinine dissolves very readily in such an alcoholic solution of sodium hydroxide, in fact about ten times more readily than in alcohol itself. This solution is added to four millimols of picric acid (0.916 gm.) dissolved in about 25 c.c. of alcohol. An orange-red precipitate forms immediately on mixing the two solutions, which darkens somewhat on standing. After standing for several hours

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\* Unfortunately another paper by Greenwald, in which he modifies this statement, has been overlooked (*Jour. Biol. Chem.*, 1928, 80, 103). The findings in the present paper support Greenwald's theory.

in a stoppered vessel, the mother liquor is removed by centrifugation, and the precipitate is washed twice with about 15 c.c. of absolute alcohol. It is then washed three times with ether. The compound obtained after drying *in vacuo* is an orange-red crystalline powder, yield 0.67 gm. This compound is referred to in the present investigation as Compound 1.

Compound 1 darkens on heating, but does not melt. It is highly explosive; 0.2 gm. heated up to 145° C. exploded spontaneously. It contains no alcohol. This compound is very readily soluble in water, forming a deep red solution. At room temperature one part of it dissolves in less than two parts of water. When such a solution is added to a large volume of alcohol, red crystals are precipitated, which, however, contain about 3.0% less picric acid than the original compound. This is probably due to some partial decomposition which takes place while the compound was dissolved in water. More dilute solutions are also red, and in shade and intensity of colour they resemble the colour obtained in Jaffe's reaction for creatinine. Such a solution on boiling or heating on the water bath loses the red colour and becomes orange-yellow. Practically complete decomposition must take place, because, if this solution is poured into alcohol, no precipitation takes place. The picric acid originally present in the compound is completely precipitated with "nitron".

The watery solutions of Compound 1 are distinctly alkaline in reaction. After destroying the red colour as much as possible by heating, the alkalinity of a sufficiently dilute solution can easily be determined by titration with acid. The figure thus obtained, expressed as sodium, indicated the presence of one atom of "free" sodium in Compound 1. But the total sodium content of the compound was found to be 11.0%, which points to two atoms of sodium in each molecule. The other analytical figures obtained are listed in Table 1. They indicate a compound consisting of one molecule of creatinine, one molecule of picric acid, and two molecules of sodium hydroxide.

#### The Formation of the Red Isomer of Creatinine Picrate.

Compound 1 dissolves in aqueous alkaline solutions and develops a deep red colour as it does in water. If, however, it is added to mineral acids of normal or greater strength,



TABLE 1.

*Analyses of Compound 1 and Red Isomer of Creatinine Picrate.*

|                            | Sodium. | Picric Acid. | Creatinine. | Nitrogen. |
|----------------------------|---------|--------------|-------------|-----------|
|                            | %       | %            | %           | %         |
| COMPOUND 1—                |         |              |             |           |
| Calculated for compound of |         |              |             |           |
| one molecule of            |         |              |             |           |
| creatinine, one of picric  |         |              |             |           |
| acid, and two of           |         |              |             |           |
| sodium hydroxide ..        | 10.9    | 54.3         | 26.8        | 19.9      |
| Preparation 1 ..           | 11.0    | 54.9         | 26.8        | 20.0      |
| "      2 ..                |         | 55.0         | 27.0        | 19.0      |
| "      3 ..                |         | 54.4         | 26.4        |           |
| RED ISOMER OF CREATININE   |         |              |             |           |
| PICRATE—                   |         |              |             |           |
| Calculated for creatinine  |         |              |             |           |
| picrate ..                 |         | 67.0         | 33.0        |           |
| Preparation 1 ..           |         | 66.8         | 32.6        |           |
| "      2 ..                |         | 67.6         | 32.2        |           |

a brilliant red crystalline compound is precipitated, while the acid turns yellow. For example, 0.4 gm. of Compound 1 is mixed with four c.c. of 2N hydrochloric acid, and the red precipitate is washed with normal hydrochloric acid, water, alcohol, and benzol; yield 0.195 gm. On heating, this red compound begins to turn orange at about 130° C. and yellow at 140° C. It melts at 206° C.; it is sparingly soluble in water, forming a yellow solution. On adding cold ethyl alcohol to this compound a strongly yellow solution is also obtained. This solution, however, contains mostly picric acid. The red compound therefore seems to decompose under this treatment. On analysis this compound was found to have a picric acid content of about 67% and a creatinine content of approximately 33%. These figures are similar to those obtained with ordinary creatinine picrate (melting point 212° C.). Judging from these analytical figures and from the properties of this red substance in general, one comes to the conclusion that one is dealing with a red isomer of creatinine picrate which is identical with the red tautomer of creatinine picrate obtained by Greenwald and Gross (*Journ. Biol. Chem.*, 1924, 59, 601).

## ANALYTICAL.

## Picric Acid.

0.05 to 0.1 gm. of the material to be analysed is dissolved and heated in about 50 c.c. of water. After the solution

has lost its red colour, it is cooled and made up to 100 c.c. An aliquot part of this solution is acidified and then neutralised with calcium carbonate. Then it is titrated with methylene blue (Bolliger, *THIS JOURNAL*, 1934, 67, 240).

#### Sodium.

About 0.2 to 0.3 gm. of compound is mixed with three c.c. of 4N hydrochloric acid in a centrifuge tube. After centrifuging down the red isomer of creatinine picrate, the supernatant fluid is transferred quantitatively into a small Kjeldahl flask. The red precipitate is then washed with normal hydrochloric acid and four changes of water. All these washings are transferred into the Kjeldahl flask. After destroying the remaining organic material with perchloric acid and nitric acid (Bolliger, *Austral. Journ. Exp. Biol. Med. Sci.*, 1932, 10, 57) one evaporates to dryness, then the residue is dissolved in water and transferred into a weighed crucible. After evaporating the water sulphuric acid is added. Then one ignites and weighs the remaining sodium sulphate.

#### Creatinine.

This was determined colorimetrically, using Folin's method (*Ztschr. f. Physiol. Chem.*, 1904, 41, 223).

#### DISCUSSION.

In the previous communication (*THIS JOURNAL*, 1936, 70, 211) it was assumed that creatinine has to be present in its enol form, in order to be capable of giving Jaffe's reaction or other similar colour reactions. In the present investigation it was observed that the solubility of creatinine in alcoholic sodium hydroxide is much greater than in alcohol alone. This observation would support the hypothesis that some rearrangement and probably enolisation takes place in the creatinine molecule due to the presence of alkali. However, simple salts of the enol form of creatinine have not yet been isolated. The red compound obtained on adding the alkaline alcoholic solution of creatinine to a picric acid solution suggests an organic molecular compound on account of the mode of its formation and on account of its colour. However, certain unusual features have to be pointed out. Ordinary compounds of this nature are formed, for example, between nitro-phenols and aromatic amines, as the compound

between picric acid and o-brom-aniline (Hertel, *Annalen der Chemie*, 1926, 451, 179). In the present case the molecular compound is formed between picric acid and some kind of a sodium hydroxide compound of enolised creatinine. The formation of some form of a sodium hydroxide compound of creatinine one has to assume, in order to explain the analytical findings. These two compounds, because of their residual valencies, emanating from the nitro groups of picric acid and from the unsaturation in the enolised ring of creatinine, form a molecular compound similar to those formed by certain nitro-phenols and aromatic hydrocarbons or aromatic amines.

On adding acid to Compound 1, both molecules of sodium hydroxide are removed from the molecule, but no further structural alterations take place. The sparingly soluble red isomer of creatinine picrate is obtained. This deeply coloured organic complex is changed by heating into the ordinary yellow creatinine picrate. Thus ultimately the residual valencies emanating from the double bond of enolised creatinine and from the nitro groups of picric acid in Compound 1 and in the red isomer are replaced by the valencies originating from the basic nitrogen group and the hydroxyl group respectively.

As pointed out before, Compound 1 is readily soluble in water. Such a solution is of a shade and intensity of colour which resembles that given by Jaffe's reaction for creatinine. This compound may therefore be responsible for Jaffe's colour reaction. On the other hand, compounds with similar properties but of somewhat different composition, are obtained by using less excess of picric acid or by working in greater alkali concentration. These compounds as compared with Compound 1 are characterised by a smaller picric acid content. It is considered that in the aqueous medium of Jaffe's reaction such compounds may also be present.

#### SUMMARY.

If Jaffe's reaction for creatinine is carried out in an alcoholic medium, an orange-red crystalline compound can be obtained, which consists of one molecule of creatinine, one of picric acid and two of sodium hydroxide. This or a somewhat similar substance may be responsible for the red colour obtained in Jaffe's reaction. Chemically it has been considered a molecular compound between picric

acid and creatinine plus two molecules of sodium hydroxide. On treatment with acid it furnishes a red isomer of creatinine picrate.

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## GEOLOGICAL NOTES ON THE COUNTRY BETWEEN THE YASS AND SHOALHAVEN RIVERS.

By M. D. GARRETTY, B.Sc.

(With Plate VIII and one text-figure.)

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(*Manuscript received, October 23, 1936. Read, November 4, 1936.*)

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The following notes have been compiled as a result of scattered observations and traverses made between 1931 and 1935. The accompanying map is intended to portray the broad relations of the rock-systems and to serve as a guide to future workers. In its preparation cognisance has been taken of the work of Carne and Jones (1919), Craft (1931) and Naylor (1935), in so far as it impinges on the area; for a detailed map of the Lake George district, see a paper by the writer (1936).

### UPPER ORDOVICIAN.

Of the several belts shown on the map, that on the east is the best known. Slates, phyllites, sandstones, grits and quartz-schists are the rock-types; in the river gorges they are fresh and resistant, while on the plateau level they are soft and much weathered, and differ considerably from the former in appearance. Graptolites were not found in the area mapped, but numerous occurrences of crustacean carapaces are very similar to carapaces found in association with Upper Ordovician graptolites lower down the Shoalhaven at Badgery's Crossing and Tallowal Gully.

Upper Ordovician graptolites have recently been described (Naylor, 1935) from I.9.\* This seems at present to be an isolated occurrence.

Fossils have not been found in the area marked as Upper Ordovician to the west of Lake George. In his paper on the Yass District (1912) A. J. Shearsby notes on his map a belt of shales extending south from Gunning to the Yass River, and he calls them the Gunning Shales;

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\* Grid reference to map.

this belt he regards as homotaxial with the Jerrawa Shales, and of Upper Silurian age, on lithological grounds, apparently. The general occurrence of phyllites, slates, schists and schistose grits, as well as strong folding and crumpling such as is found on the Shoalhaven River, has guided the writer in regarding these rocks as Upper Ordovician. The rocks are much more altered than the Silurian to the east—both the Upper Silurian of Mount Fairy and the possible Lower Silurian of Collector. Moreover, in this extensive belt there is a total absence of limestones, which is strong circumstantial evidence in view of the common association of this rock with the known Upper Silurian belts.\* What is undoubtedly a remnant of the same belt is found at Cullarin, 9.C.

The evidence is overwhelming that the Ordovician rocks form a closely folded unit. Innumerable sections exposed by the Shoalhaven and its tributary creeks point definitely to isoclinal folding, and the same conclusion is reached from numerous strike and dip determinations on the plateau level; only a few such are shown on the map.

#### LOWER SILURIAN.

Naylor describes Lower Silurian fossils from near Bungonia (p. 124) in rocks which "appear to dip under a more arenaceous formation of Upper Ordovician age" to the west. This is the only definite Lower Silurian area in the region under discussion, and according to Naylor's section (p. 128) it would seem as if the Lower Silurian may be expected in a narrow zone only. The zone to the east of Lake George marked on the map as being of "doubtful age" should perhaps be mentioned here. No fossils have thus far been found in this belt, other than rain-prints and ripple mark in D.7, and one is reduced again to tentative lithological correlation. While there does not seem sufficient evidence to suggest an Ordovician age, since the rocks do not show the degree of regional metamorphism and folding exhibited to the west of the Lake, there is on the other hand a distinct appearance of greater age when compared with the Mount Fairy (Upper Silurian) Series to the east. Whatever be their age, there seems no doubt

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\* Since the above was written, Upper Ordovician graptolites have been collected from the Jerrawa shales by Mrs. K. M. Sherrard (*Proc. Linn. Soc. N.S.W.*, 1936, 61, Abstract of Proceedings, 1).

that the rocks of this belt will be found to have preceded those of the Mount Fairy Series. The writer has in a recent paper (1936) suggested that the amphibolites of the eastern margin of Lake George may be pre-Upper Silurian, which would imply that the associated injected sediments would be at least as old, though no attempt is made in that paper to subdivide the sediments. The boundary between this doubtful zone and the Mount Fairy Series on the accompanying map has been so drawn as to include, (i) the amphibolite-bearing areas, (ii) areas near Lake George which in the field present a rather more ancient appearance than the Mount Fairy Series, including outcrops in E.5, E.4, E.3 and F.4, and (iii) a zone exposed in the Travelling Stock Reserve, F.9-10, just east of Yarra, which is very similar to that in F.4.

#### UPPER SILURIAN.

The Upper Silurian rocks occur in two belts, very probably the opposite limbs of a large fold structure, and are among the best known strata of the region. The belt running from K.10 south to J.4 was examined mostly in its northern section. The limestones occurring between Bungonia Creek and Bungonia, K.9-10, have been described by Carne and Jones (1919). They are definitely of Upper Silurian age. Further south, an Upper Silurian cyathophylloid form was found in a mass of silicified limestone, and, nearby, shelly fossils in fine sandstone; these included chonetoid types considered by the late Mr. W. S. Dun to be of Upper Silurian age. This locality is marked on the map as fossiliferous, in the south-western corner of K.8. Further south still, near Windellama, in J.6, occur beds of limestone regarded as Upper Silurian by Carne and Jones; this age was also confirmed by Mr. Dun after examination of fossils collected by the writer. As at Bungonia (and further north at Marulan), the Windellama limestone consists of two belts (see Fig. 1).

With regard to the age of the belt stretching to the south of Goulburn, we have the northwards continuation through the Upper Silurian limestones of Baw Baw and elsewhere; to the south we have a belt of definite Upper Silurian limestone extending for about nine miles south of Mount Fairy. Other fossils are not known from this belt. Apart from limestones, the Upper Silurian sediments are chiefly shales and fine sandstones. Occasionally a tendency to slaty or phyllitic forms is noted. As with the older

systems, there is every evidence that close isoclinal folding has taken place; this is dealt with in detail in the paper on the Lake George District.

#### DEVONIAN.

There appear to be representatives of both Middle and Upper Devonian in this region, but these are not distinguished on the present map. The writer (1936) has already described the best known of the Middle Devonian occurrences—that near Tarago, G.4. *Favosites* sp. and *Receptaculites australis* were taken as indicating the Middle Devonian age of a group of limestones which appear to underlie a synclinal structure of red-bed conglomerates, sandstones and quartzites, and felsites, some of which are doubtless Upper Devonian. Further north, at Lake Bathurst, the writer has collected numerous fossils from several limestone horizons. This assemblage includes *Receptaculites australis*, and some brachiopods of Devonian aspect. There is also evidence of the red beds again hereabouts. Other narrow limestones and calcareous olive shales occur in creeks to the south-west of Tarago township, and these have been provisionally regarded as also Middle Devonian. But it is not impossible, especially in view of the rather sharp folding of these latter beds, that they are inliers of Upper Silurian exposed by down-cutting through the Devonian. It will be noted that the occurrence is directly on the line of the known Upper Silurian belts in this district.

In the neighbourhood of Tarago the limestones are followed by red conglomerates, and then a group of massive quartzites and felsites, which form prominent peaks and ranges. This is similar to the succession near Goulburn, where red beds of the same type are seen to underlie the quartzite mass of Governor's Hill.

Another belt of Upper Devonian, divided by an elongated granite intrusion, is to be found near Bungonia. The rock types include sandstones, tuffs, slates, and possibly igneous flows. From Bungonia to Windellama, I.6, the rocks are distinctly different in type from those of the Silurian and Ordovician nearby, and moreover, have much shallower dips. Naylor (1935) seems rather inclined to doubt the existence of Upper Devonian (Lambian) rocks in the vicinity of Bungonia. However, fossils have been collected from several localities. In J.9, fossils are rather scarce in the sandstones, but casts of brachiopods and lamelli-



branches were obtained, and identified by the late Mr. W. S. Dun as of definite Upper Devonian age. Moreover, at a point further south, on Jacqua Hill, J.8, fossils were obtained in ripple-marked sandstone; these include *Lepidodendron australe* and other forms, stated by Mr. Dun to be indubitably of Upper Devonian age. Thus, even were the sandstones on the Bungonia-Goulburn road not Upper Devonian, the structure suggested by Naylor would still have to accommodate the Upper Devonian at Jacqua Hill. Shelly fossils may also be found on Lumley Creek, in central J.9.

Another question raised by Mr. Naylor is that of the age of the limestone on Jerrara Creek, south-western J.10. A Devonian age was suggested by Carne and Jones (1919), but it has been provisionally classed by Naylor as Upper Silurian (p. 126), a conclusion which apparently he did not find to conflict with his conception of the structure, for he states: "These limestones dip to the west along with all the other series in this part of the district. They therefore appear to underlie the Jerrara Series [Lower Silurian], and though the latter has not yet been traced as far north as portion 46, the overlying Upper Ordovician belt has been identified (both lithologically and palæontologically), in portions 270 and 271, ph. Jerrara, a little to the west of the most northerly outcrop of limestone." While the writer also examined the limestone outcrops, and failed to find diagnostic fossils, and would prefer to retain an open mind on the question of their age, it is interesting to consider the implications in each case. The southernmost limestone outcrop lies to the east of the fossiliferous horizon\* of the Lower Silurian, and thus dips could take it under the Lower Silurian without difficulty. As, however, on Jerrara Creek the Ordovician occurs a little to the west of the limestone, it leaves scant room for the Lower Silurian, which occupies a quarter of a mile on the road. While the writer is well aware that contour, thinning of beds, and the incidence of isoclinal folding may considerably affect width of outcrop, he has not as yet a clearly defined mental picture of a succession of Upper Silurian limestone, Lower Silurian and Upper Ordovician at this point, especially in view of the variable dips and strikes. The

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\* Boundaries of Lower Silurian and Ordovician, and the fossil-bearing locality, are transferred from Naylor's map.

line of the limestone outcrops and the strikes of the rocks to the east of them, including the fossiliferous Devonian, are west of north, while the few strikes taken in the Lower Silurian are meridional or somewhat east of north. Should the limestone turn out to be Devonian in age after all, no radical alteration of structure would become necessary, for the writer's conception of the Upper Devonian of the region is that it is only a residual veneer, and that down-faulting need not always be called into play to explain isolated occurrences.

An area, extending from the Goulburn-Bungonia road southwards past Lake Bathurst has been left blank on the present map. This was previously regarded by the writer as of Devonian age. At various localities rocks were observed which seemed most closely related to the Upper Devonian. In particular, for some miles towards Bungonia from Goulburn, tuffs, felsites and shales were observed similar in appearance to the Upper Devonian on Bungonia Creek. However, no palæontological evidence one way or the other is to hand, and since Mr. Naylor regards much of the stretch between Goulburn and Bungonia as Upper Silurian, it has been thought wisest to defer consideration of this zone. Outcrops are poor in this region.

On the maps of the geological survey Devonian rocks are shown as outcropping on the eastern bank of the Shoalhaven in the vicinity of L.8. I have not examined this eastern side of the Shoalhaven in very great detail, but have no doubt that outcrops of Devonian rocks of any size do not occur, Ordovician and Kamilaroi being the only systems found. Their strike, if meridional, would carry them into the belt marked as Devonian on these maps between Yalwal Creek and Badgery's Crossing. These outcrops are not shown on the present map, as the writer believes that they do not exist, since he has found Ordovician rocks continuing downstream, which are unconformably overlain by Devonian only to the east of the Kangaroo River.

#### KAMILAROI.

Strata of this age occur only in the extreme north-east of the area, forming cliffs at intervals along the eastern bank of the Shoalhaven River.

### TERTIARY.

Chief among the Tertiary sediments are the high-level gravels and clays occurring in belts parallel to the Shoalhaven (see papers by Craft). Tertiary lacustrine deposits also occur, and include deposits of laterite, and fine sandstones altered by contact metamorphism by later basalt flows. Laterite is found chiefly in I-J.8, K.7 and G.4. Manganese, cobalt and nickel-bearing Tertiary sands are also common in isolated patches for some miles south of Bungonia. Plant fossils are found in the Tertiary beds in K.10, and in contact quartzite near the silicified limestone in south-western K.8. Tertiary basalts are common, in scattered residual patches, as in J.9, I.8, K.8, I.6, G.4 and F.10.

### IGNEOUS ROCKS.

#### Amphibolites.

The occurrence of these has been fully dealt with elsewhere by the writer (1936); it is suggested that they probably represent basic intrusives of pre-Upper Silurian age.

#### Granites.

It is quite certain that granites of at least two ages are present in the region, but the age of the individual bosses is in many cases obscure. Each will be dealt with separately.

All that can be said of the granites west of Lake George is that they apparently cut sediments of Upper Ordovician age; no upper limit of age can be given. The rocks vary from hornblende-biotite-granites to quartz-felsparporphyries. Strong crushing of the rocks is in evidence. At the contact with the slate tongue near Cullarin, excellent sections of various stages of assimilation of sediment by gneissic granite may be seen in large road-cuttings; all stages of transition are found.

The writer has elsewhere given reasons for assigning an epi-Silurian age to the granite on the eastern shores of Lake George, and the same doubtless applies to the mass just east of Bungendore. Partly digested masses of amphibolite may also be found in the latter. It is probable also that the Wologorong mass, E.7-8-9, is a similar continuation of this epi-Silurian granite northwards. It is chiefly a crushed biotite-hornblende granite, with

abundant micropertthite. Amphibolite masses may likewise be found in this granite.

The Boro Ganite, H.1-5, may easily be of later age. Although sheared zones occur, uncrushed hornblende-biotite-granite with no trace of directional structure is quite common. It is considered that this granite may be of epi-Devonian age.

The Bungonia granite, K.8, with which may be linked the Nerrimunga Creek intrusion, L.8, appears to be definitely of epi-Upper Devonian age. Transgressive relations with the Upper Devonian are found on Bungonia Creek. Granite at Bungonia itself grades northwards into porphyries and porphyrites towards Jerrara Creek and to the north-east. Southwards granodiorite is found, and towards the western margin aphanitic types again occur. Biotite is the chief ferromagnesian mineral of the granite. The Nerrimunga Creek intrusion exhibits pronounced differentiation, with formation of hybrids between earlier and later types.

Metamorphism by the Bungonia granite is more pronounced than was observed in the others. The silicified limestone five miles south of Bungonia may be due to the granite intrusion. Nearer the junction, quartz-pyroxene hornfels may be found at the dip arrow about one and a half miles south of Bungonia; the rock also contains titaniferous magnetite. Biotite-cordierite hornfels occurs on the western boundary of the granite in J.8. Altered rocks such as cordierite hornfels are common near the Nerrimunga Creek mass.

#### Quartz-Dolerite Dykes.

These are very common in the area, especially in the eastern division, and are exposed chiefly as dykes cutting the older Palaeozoic rocks in the gorges of the Shoalhaven and its tributaries. The average width is about five feet, and there is a tendency to occur in clusters. Several distinct types are found, which it is hoped to describe more fully later. All that can be definitely stated as to their age is that they are post-Silurian.

#### STRUCTURAL GEOLOGY.

Sufficient is not known of the structure of the region to justify an attempt to draw sections across the map. It will be sufficient to point out a few significant features which may be found useful in correlating with other areas.

The Ordovician and Lower and Upper Silurian are individually closely-folded units. Regionally, it is probable that some such structure as Naylor has postulated further north may be found to exist. It is suggested that Goulburn-Tarago may be the axis of a major synclinal structure embodying the Ordovician, Silurian and later the Devonian units. While Naylor has found evidence for a continuation of such a structure north from Goulburn, it is probable that it is too simple an explanation for the Lake George region. One outstanding difficulty is the amphibolite series—unless we assume that the basic intrusions were fairly confined, and then we might have a succession Ordovician-? Lower Silurian-Upper Silurian-Devonian eastwards to Tarago. But there is not much evidence to support this, and conditions on the east are not so simple. The dominant westerly dip over the whole area of the older rocks seems to favour a system of major folds having axial planes dipping in this direction also, the bedding and schistosity of the smaller crumples and folds being indicative of the larger structures, and supporting some such interpretation as Naylor has given west from Bungonia. An examination of the Upper Silurian limestone occurrences is of interest (see Fig. 1). In each of the four cases given, Mount Fairy, Windellama, Bungonia and Marulan, there is a main belt and a subsidiary belt (which may divide as at Bungonia). If we assume a correlation of the main belts, it is seen that there is an overturned relationship between the Windellama and Marulan-Bungonia deposits. At Bungonia the main belt is on the very east, near the Ordovician; at Windellama it is shown as being on the very west, though the field relations here are not so clear. We thus have features which, although of an unknown degree of reliability, are not opposed to the interpretation that at Bungonia and Windellama we have the main (nearly basal) limestone outcropping on the eastern and western limbs respectively of the asymmetrical syncline shown on the right of Naylor's section. Should the Jerrara Creek limestone be Silurian, it would correspond in position with the Windellama limestone. The Mount Fairy limestones (normal sequence) would appear to represent the western limb of the overfold as it descends again to earth.

It is likely that the Upper Devonian does not share the large-scale overfolds of the earlier systems, which were

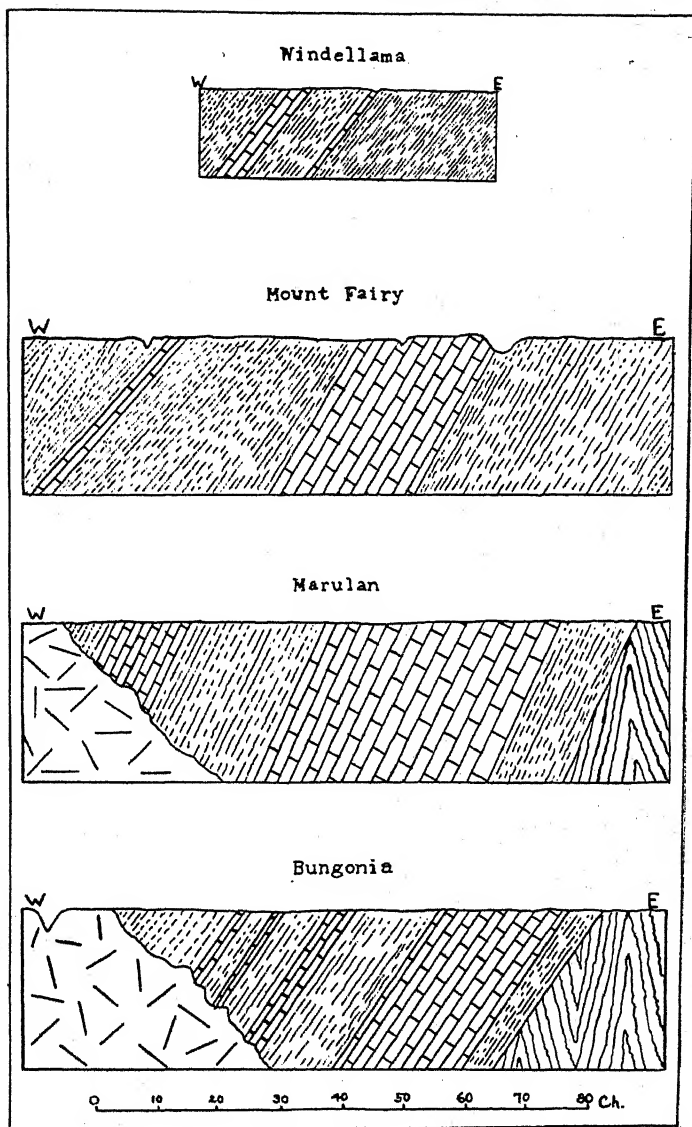
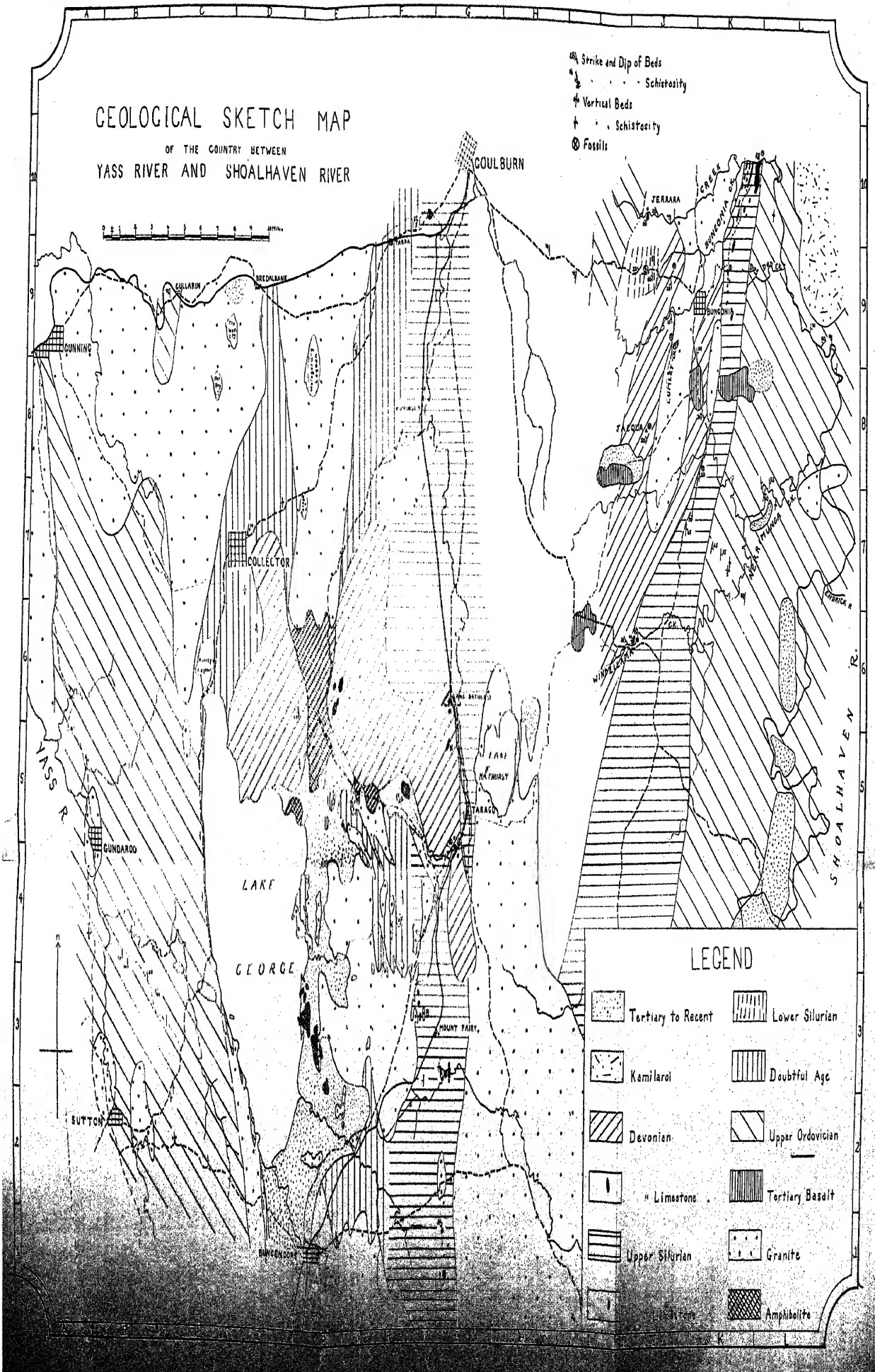


Fig. 1.

Sections illustrating the size and sequence of limestone deposits at Windellama, Mount Fairy, Marulan and Bungonia, the last two after Carne and Jones (1919).







THE OCCURRENCE OF A NUMBER OF VARIETIES  
OF *EUCALYPTUS RADIATA* (*E. NUMEROSA*)  
AS DETERMINED BY CHEMICAL ANALYSES  
OF THE ESSENTIAL OILS.

PART II.

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In continuation of our investigation into the varieties of *Eucalyptus radiata* (*E. numerosa*) as determined by chemical analyses of the essential oils,<sup>1</sup> we raised a number of plants from seed collected near Nullica, via Eden, in November, 1931. The leaves and terminal branchlets of several of these trees were cut and subjected to steam distillation. The essential oils thus obtained gave the chemical and physical constants set out in the accompanying table.

The results obtained confirm the constancy of the several forms or varieties, but a remarkable observation was made with a tree planted from seed of the form called Variety A. In this particular instance two stems grew from the one root system. The leaves and terminal branchlets from each stem were separately distilled, when the essential oils were found to differ from one another in chemical composition. One yielded an oil containing 50 per cent. piperitone, identical with Variety A, and the other yielded an oil containing only 18 per cent. piperitone with a considerable quantity of piperitol and, consequently, it bore a very close resemblance to what we prefer to regard as the type. Although the type contains usually only about 5 per cent. piperitone, a reference to Table "B", page 186, *THIS JOURNAL*, 1932, 66, reveals the occurrence of intermediate forms between the type and Variety A containing up to 18 per cent. piperitone.

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<sup>1</sup> *THIS JOURNAL*, 1932, 66, 181-193.

*Essential Oil from Tree of Eucalyptus radiata, Type.*

| Weight of Leaves. | Yield of Oil. | $\frac{15}{d_{15}}$ | $20^{\circ} a_D$ | $20^{\circ} n_D$ | Solubility in 80% Alcohol. | Pipertone Content. | Phellandrene. | Remarks.  |
|-------------------|---------------|---------------------|------------------|------------------|----------------------------|--------------------|---------------|---|
| lbs.<br>18        | %<br>2.3      | 0.8315              | -43.7°           | 1.4778           | 1.5 vols. (by weight).     | %<br>3             | Abundance.    | Tree 27' 3" high. Diameter 4" at 2' 9" from ground level. Cut 13/11/1935. |

*Essential Oils from Tree of Eucalyptus radiata, Variety A.*

| Stem No. 1 | 3½  | 1.9 | 0.8983 | -34.5° | 1.4792 | 1.2 vols. 70% alcohol (by weight). | 18 | Moderate quantity. | Stem 16' 7" long. Diameter 1½" at 2' 7" from ground level. Cut 17/9/1936. |
|------------|-----|-----|--------|--------|--------|------------------------------------|----|--------------------|---|
| Stem No. 2 | 15½ | 2.4 | 0.9051 | -56.2° | 1.4799 | 1.1 vol. 70% alcohol (by weight).  | 50 | Abundance.         | Stem 20' long. Diameter 3½" at 2' 7" from ground level. Cut 17/9/1936.    |

There was considerable difference in the content of piperitone and piperitol in the respective oils. The odours were also dissimilar, one resembling *Eucalyptus dives* rich in piperitone, whilst the other had the characteristic fragrant odour associated with *E. radiata* type.

It is noteworthy that the weight of foliage and yield of oil obtained from No. 2 stem were considerably greater than those obtained from No. 1.

We are unacquainted with any record of a similar observation.

It was our intention merely to record this observation without comment. We feel, however, that the far-reaching influence of this observation cannot be over-emphasised and, consequently, we are justified in directing attention to its probable effect on the botanical nomenclature of the eucalypts.

We have already directed attention<sup>2</sup> to the undesirable practice of certain botanists of describing new species and varieties of economic plants on very slender morphological evidence. In our original paper we stressed the fact that the varieties of *Eucalyptus radiata* could not be separated from the type on morphological evidence. Before making this statement we obtained confirmation of this view from our botanical colleagues, Messrs. E. Cheel and M. B. Welch. Despite this evidence, Mr. W. F. Blakely, in a subsequent publication, "A Key to the Eucalypts" (1934), described our Variety A as *Eucalyptus Lindleyana*, var. *stenophylla* (page 209).

In view of the apparent absence of definite morphological evidence, we can only assume that Mr. Blakely used our chemical data as a basis for separating and describing this supposed variety. It is perfectly clear from our work on the physiological forms of well-known species of eucalypts that it is a dangerous practice to use differences in chemical composition alone as a basis of classification.

The very important observation described in this paper provides definite confirmation of our contention that Mr. Blakely's variety *stenophylla* does not exist. The evidence submitted shows that *E. radiata* (*E. numerosa*) and Blakely's variety *stenophylla* have been found growing together on one and the same plant.

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<sup>2</sup> THIS JOURNAL, 1930, 64, 218-223; 1936, 70, 1-38.

SPECIES OF *HELMINTHOSPORIUM* AND  
*CURVULARIA* ASSOCIATED WITH  
ROOT-ROT OF WHEAT AND OTHER  
GRAMINACEOUS PLANTS.

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(With Plate IX and three text-figures.)

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The importance of *Helminthosporium* as an agent in the causation of root diseases of graminaceous plants has long been recognised, but no paper has hitherto been published in which reference is made to all species of the genus that have been found in association with root-rot of wheat. In the following paragraphs attention is drawn to the several species so far described, together with the writer's observations on the morphology of forms isolated in Australia, and reference is also made to the genus *Curvularia*, which was established by Boedijn in 1933<sup>(3)</sup> and which includes several fungi previously classified in *Helminthosporium*, *Brachysporium* and other genera.

The genus *Helminthosporium* was defined by Link in 1809,<sup>(11)</sup> and brief descriptions of numerous species of this and the related genus, *Brachysporium*, are given in the works of Saccardo. A study of the literature on fungi associated with root-rot diseases of cereals has shown, however, that seven distinct species of the genus *Helminthosporium* have been isolated by various workers from foot-rot-affected wheat. For convenience, these might be divided into (a) the large spore group, and (b) the small spore group. The species falling into each group are as follow :

(a) LARGE SPORE GROUP.

(1) *H. bicolor* Mitra. This species was described by Mitra<sup>(13)</sup> in 1930. He states that the spores are greyish

to dark greyish-smoky brown in colour, are typically cylindrical with abruptly rounded ends, are straight or slightly curved, and are 1-9 septate (av. 5); that the mean size is  $51 \times 14$  microns, the extremes being  $16.5-79 \times 10-20$  microns. The species was isolated in India, and was found to be capable of producing pronounced foot- and root-rot in wheat and barley seedlings.

(2) *H. halodes* Drechs., var. *tritici* Mitra. This new variety was also described by Mitra<sup>(13)</sup> in 1930. His observations showed that it differed from the main type in regard to spore size and septation. The extreme measurements are given as  $23-73 \times 13-20$  microns, the mean size being  $52 \times 16.5$  microns. This species was also isolated in India, and in inoculation tests proved to be virulent on seedlings of wheat and barley.

(3) *H. pedicellatum* Henry. This fungus was isolated from a diseased wheat root in Minnesota, U.S.A., by Henry, and was described in 1924,<sup>(8)</sup> the cultural and morphological features being fully outlined. The conidia measured  $65.3 \times 23.4$  microns, and were for the most part 7-septate. The species was found to be only weakly parasitic.

(4) *Helminthosporium* N Henry. A type differing from *H. sativum* sufficiently to be regarded as a distinct species was also isolated by Henry<sup>(8)</sup> in 1923, at Minnesota, principally from seeds. The conidia are stated to be much narrower and more cylindrical than those of *H. sativum*, and resemble the spores of *Podosporiella verticillata* O'Gara. No synnemata, however, developed in culture. Henry determined the means for length, width and number of septations to be 64.2 microns, 14.0 microns, and 7.28. He found in inoculation tests that this species was less virulent than *H. sativum*. The identity of the fungus was not established.

(5) *H. sativum* P.K.B. This is the most common species of *Helminthosporium* found in association with root-rot conditions in wheat. In Australia it has been isolated<sup>(10)</sup> from wheat, oats, barley, rye and several grasses, and has been obtained from material from the Federal Capital Territory and all States, excepting Tasmania. Drechsler,<sup>(6)</sup> who has critically reviewed the nomenclature of *H. sativum* and has pointed out where early workers were in error in

assigning other specific names to *Helminthosporium* isolated from diseased wheat, concludes that "for the most part a single species of *Helminthosporium*, namely *H. sativum*, is involved in the widespread infection of wheat manifested variously by such symptoms as stunting of growth, seedling

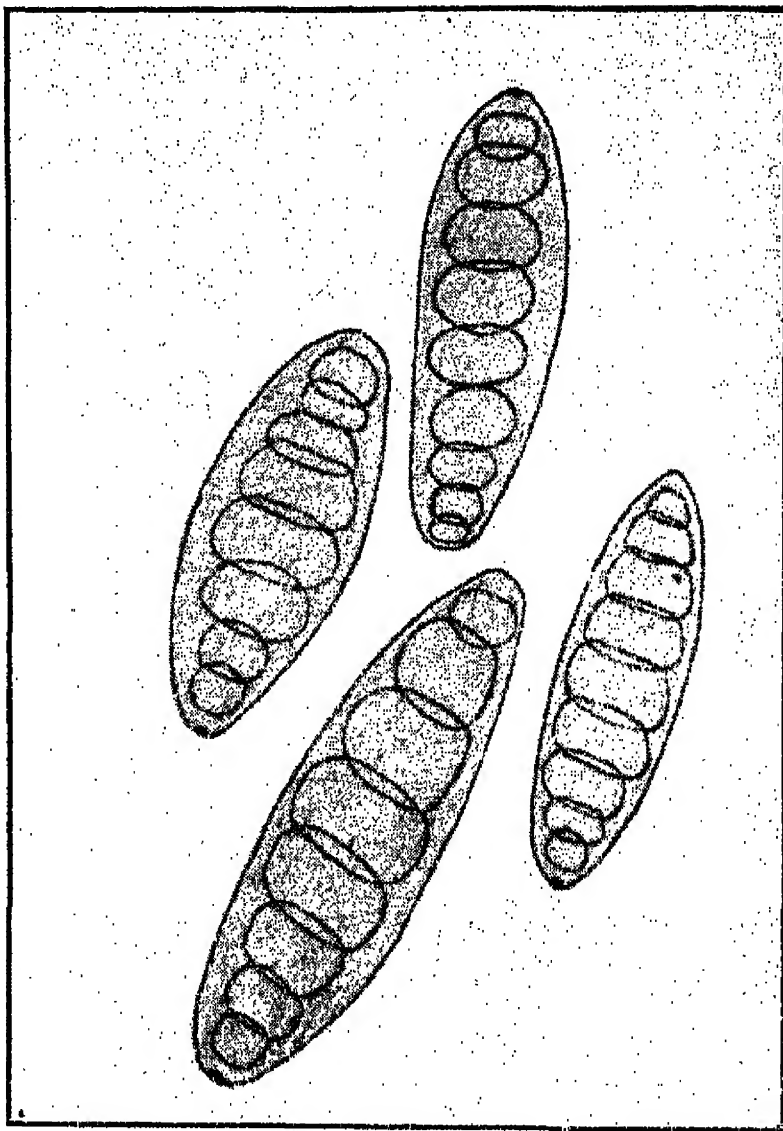


Fig. 1.—Conidia of *Helminthosporium sativum* P.K.B.  $\times 800$ .  
(From cultures on potato dextrose agar at 20° C.)  
(Photo by P. R. Maguire.)

blight, basal browning, root rot, foot rot, node decay, leaf spot, stem discolouration, and black point".

This species was first described in 1910 by Pammel, King and Bakke,<sup>(14)</sup> and the morphological characters of

the species have since been closely studied by a number of workers.<sup>(4) (5) (6) (7) (13) (17)</sup>

Although *H. sativum* was first isolated in Australia in 1913, and a number of papers have been published dealing with its parasitism and control, no detailed work on the morphology of the species has so far been published in this country. The writer has made a close study of the fungus in respect of pathogenicity and cultural reactions of physiologic forms<sup>(10)</sup>, and has studied its morphology under different environmental conditions. From this work, and from the reports also of overseas authorities who have examined cultures from local material, there is no doubt that the large-spored *Helminthosporium* associated with wheat root-rot throughout Australia is predominantly, if not exclusively, *H. sativum* P.K.B. (Fig. 1.)

In studying the dimensions of conidia for comparative purposes it is important to standardise the conditions of culture. Dosdall<sup>(5)</sup> observed that while temperature exerted an effect on the mean length of spores when potato dextrose agar was used, the greatest difference in length occurred between spores produced on different sub-strata. Hence, at 24° C. the mean length of conidia produced on potato dextrose was 65·75 microns, on autoclaved ripe barley heads was 67·74 microns, and on green barley leaves was 83·14 microns.

Apart from colour, shape and mode of production, the most important features in a study of spore morphology of species of *Helminthosporium* are length, width and number of septations. Stevens<sup>(17)</sup> introduced the concepts "coefficient of longitudinal eccentricity" and "coefficient of cylindricity" for more accurate descriptions of species in respect of conidial shape, but these do not appear to have been adopted by other workers to any extent.

Therefore, for the writer's studies on conidial morphology of Australian isolates of *H. sativum*, all monosporous cultures were developed under controlled conditions, and attention was given mainly to the dimensions and number of septa. In the preliminary work, conducted several years ago, only 25 conidia of each of three isolates were studied, the spores having been produced under "standard conditions" on washed agar and wheat shoots at 25° C., as defined by Stevens.<sup>(17)</sup> The results are set out in Table 1.

TABLE 1.

*Summary of Measurement Data of 25 Conidia of each of Three Monosporous Isolates of H. tetramera (Curvularia spicifera) and of H. sativum, Cultured on Sterilised Wheat Shoots on Washed Agar at 25° C.*

| Species and Strains.        | Means for—            |                      |                  |
|-----------------------------|-----------------------|----------------------|------------------|
|                             | Length.<br>(Microns.) | Width.<br>(Microns.) | No. of<br>Septa. |
| <i>H. tetramera</i> A .. .. | 23.4                  | 8.5                  | 3                |
| " B .. ..                   | 23.6                  | 8.8                  | 3                |
| " C .. ..                   | 25.1                  | 9.0                  | 3                |
| <i>H. sativum</i> A .. ..   | 76.4                  | 21.8                 | 7.4              |
| " B .. ..                   | 69.7                  | 21.9                 | 7.1              |
| " C .. ..                   | 62.1                  | 19.4                 | 5.9              |

TABLE 2.

*Measurements of 100 Conidia of each of two Monosporous Isolates of H. sativum Cultured on Sterilised Wheat Heads at 20° C.*

## ISOLATE 1.

| Septation<br>Class. | Frequency.<br>% | Range.<br>(Microns.)  | Mean.<br>(Microns.) |
|---------------------|-----------------|-----------------------|---------------------|
| 2                   | 1               | —                     | 51.1 × 23.1         |
| 3                   | 4               | 34.6–44.5 × 18.1–23.1 | 40.4 × 20.2         |
| 4                   | 4               | 42.9–51.1 × 19.8–23.1 | 45.3 × 21.8         |
| 5                   | 6               | 49.5–56.1 × 19.8–23.1 | 53.9 × 21.7         |
| 6                   | 12              | 49.5–77.5 × 18.1–26.4 | 61.0 × 22.4         |
| 7                   | 24              | 46.2–82.5 × 19.8–26.4 | 67.5 × 22.4         |
| 8                   | 26              | 66.0–85.8 × 21.4–26.4 | 75.9 × 24.0         |
| 9                   | 18              | 70.9–85.8 × 21.4–28.0 | 78.9 × 24.0         |
| 10                  | 5               | 80.8–85.8 × 23.1–24.7 | 83.1 × 24.4         |

## ISOLATE 2.

|    |    |                       |             |
|----|----|-----------------------|-------------|
| 3  | 2  | 33.0–37.9 × 14.8–16.5 | 35.4 × 15.6 |
| 4  | 2  | —                     | 52.8 × 24.7 |
| 5  | 3  | 52.8–66.0 × 19.8–24.7 | 57.2 × 22.5 |
| 6  | 14 | 52.8–77.5 × 18.1–24.7 | 60.2 × 21.4 |
| 7  | 30 | 49.5–80.8 × 18.1–26.4 | 66.4 × 21.7 |
| 8  | 29 | 66.0–85.8 × 21.4–26.4 | 76.1 × 24.4 |
| 9  | 16 | 69.3–82.5 × 19.8–26.4 | 77.0 × 24.3 |
| 10 | 3  | 77.5–82.5 × 23.1–26.4 | 80.8 × 24.7 |
| 11 | 1  | —                     | 85.8 × 23.1 |

Mean length and width of the 100 conidia of isolate 1 : 68.8 × 23.1 microns.

Mean length and width of the 100 conidia of isolate 2 : 69.5 × 23.0 microns.



A more detailed study, however, has recently been made of two isolates cultured on sterilised wheat heads in test tubes at 20° C. Since Stevens<sup>(17)</sup> has shown that humidity influences the relative variability of *Helminthosporium* spores, a representative conidial sample of each isolate for examination was obtained by taking small amounts of spores from each of three triplicate tubes and mounting them in water. The measurement data are given in Table 2, from which it will be seen that for each isolate the septation classes of highest frequency were 7 and 8, the mean dimensions for each 100 conidia being  $68.8 \times 23.1$  microns and  $69.5 \times 23.0$  microns. The mean length increased with increasing number of septa. These data are in agreement with results published by other workers. The method here adopted for presentation of measurements of *Helminthosporium* gives a clearer picture of spore size in relation to number of septa than in the case of methods adopted by most other investigators. The colony growth of two virulent strains of *H. sativum* on potato dextrose agar is illustrated in Plate IX.

#### (b) SMALL SPORE GROUP.

A number of small-spored types of *Helminthosporium* have been isolated by various workers from root-rot affected wheat,<sup>(2) (8) (9) (10) (12) (15) (16)</sup> but only in a few cases have specific determinations been given. It appears from a study of the literature that only two particular small-spored types have been closely studied, viz. the two species which have been used by the writer in infection studies already described,<sup>(10)</sup> and which have been designated, both here and abroad, as *Helminthosporium M* and *H. tetramera*. Each of these will now be considered in detail.

(1) *H. tetramera* McKinney. This species was isolated by McKinney from foot-rot-affected wheat in Oklahoma, U.S.A., in 1923. McKinney demonstrated that it was capable of attacking the roots and stem bases of winter wheat, causing injury similar to that produced by *H. sativum*, but he doubted whether the new fungus was an aggressive parasite. The species was named and described in 1925.<sup>(12)</sup> It has since been isolated from wheat in Australia<sup>(10)</sup> and in East Africa,<sup>(2)</sup> and the results of infection tests in each instance have shown that it is unimportant pathogenically. The cultural characters of

*H. tetramera* on different media at different temperatures have already been described by the writer.<sup>(10)</sup>

A study of the morphological characters of the fungus when grown on potato dextrose agar at 20° C. (cf. Fig. 2)

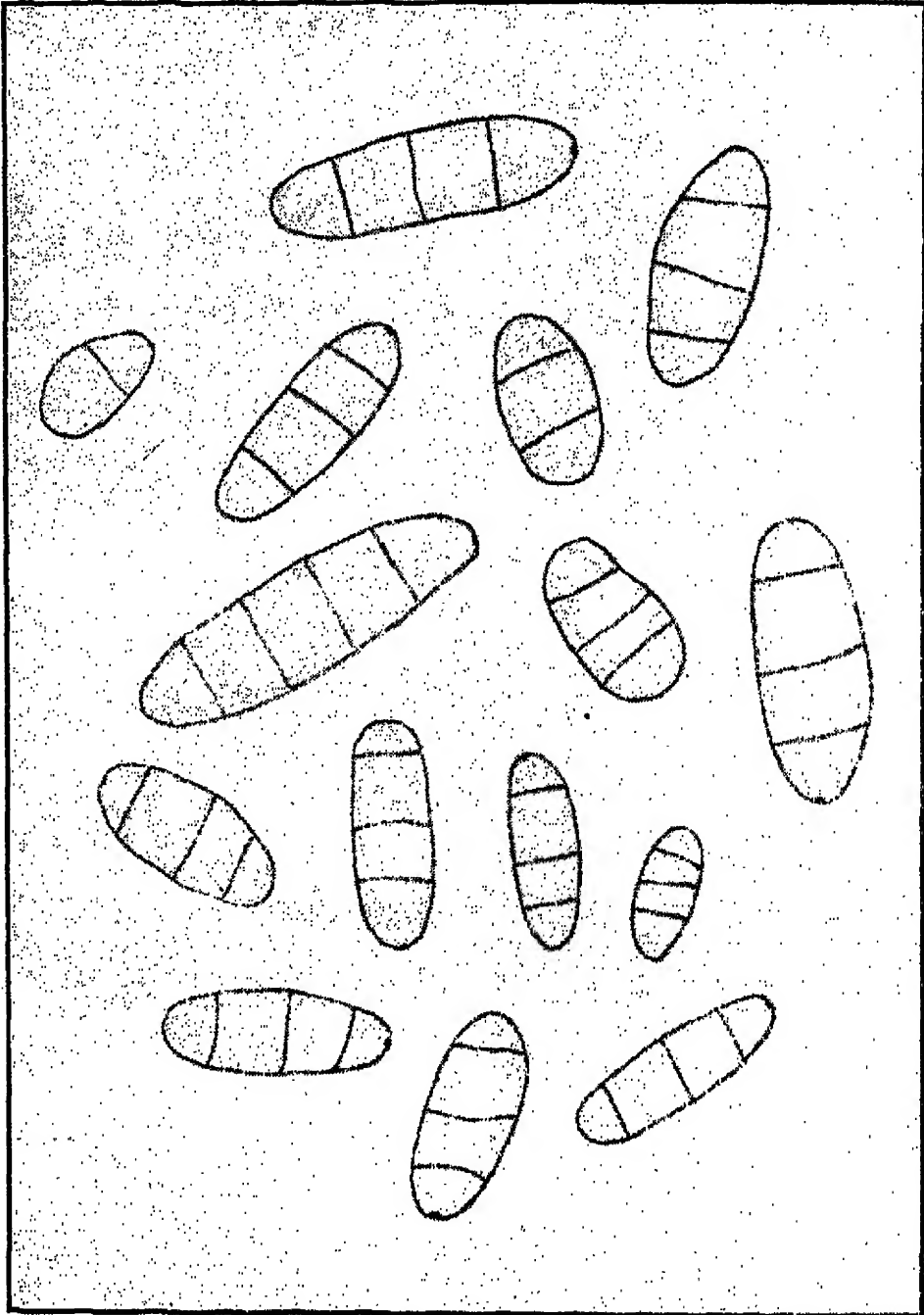


Fig. 2.—Conidia of *Helminthosporium tetramera* McKinney (*Curvularia spicifera* (Bainier) Boedijn).  $\times 800$ .  
(From cultures on potato dextrose agar at 20° C.)  
(Photo by P. R. Maguire.)

shows that the conidia are borne in clusters in varying numbers on conidiophores which are brownish in colour. The spores are oblong and symmetrical in shape, with rounded ends, and are of uniform, straw-brown colour. They are predominantly 3-septate, the septa not being as prominent as in *Helminthosporium M.*, and the spore wall not being constricted at the septa. A tiny black stipe—which connects the conidium with the conidiophore—is to be seen at the basal end of the spore. The protoplasts are smaller than in the case of *Helminthosporium M.*, so that the space occupied by the endosporium between the protoplasts and the episporium, and between the individual protoplasts is greater than with *Helminthosporium M.* The features of the episporium or outer conidial wall and the endosporium of *Helminthosporium* have been fully discussed by Stevens.<sup>(17)</sup>

The conidia germinate readily in tap water, frequently from both ends, and occasionally also from the side of the spore. Conidia kept under dry conditions in test tubes in the laboratory for 31 months germinated vigorously when placed in water.

In view of the comparative unimportance of *H. tetramera*, no extensive spore measurement studies have been made by the writer. Twenty-five conidia of each of three monosporous isolates from oats, barley and rye have, however, been measured, the spores having been produced under "standard conditions" on sterilised wheat shoots on washed agar at 25° C., as described by Stevens.<sup>(17)</sup> The data are summarised in Table 1, from which it will be seen that the approximate size of conidia of this fungus is 23·5–25 × 8·5–9 microns, based on a limited number of measurements. McKinney<sup>(12)</sup> found that "30·6 microns was the most common length" and "13·6 microns the most common width", the spores being chiefly four-celled. He does not state, however, under what conditions the conidial material was produced, nor how many spores were measured. Presumably he studied conidia taken direct from affected plants, when they would be larger than those produced on artificial media.

The fungus has been isolated by the writer from diseased roots of wheat, oats, barley and rye in New South Wales, and was first isolated in 1923. It has also been obtained from material from South Australia. Mr. E. W. Mason, of the Imperial Mycological Institute, England, has examined cultures from local material and has confirmed

the writer's determination of *H. tetramera* McKinney, but Dr. K. B. Boedijn, Java, identified the same cultures as *Curvularia spicifera* (Bainier) Boedijn, of which *Brachycladium spiciferum* Bainier is a synonym<sup>(3)</sup>. The description of this latter species was published in 1908,<sup>(1)</sup> the fungus being obtained on "brambles of dead wood". Bainier was unable to obtain perithecia or sclerotia of this fungus on artificial media, but McKinney reported that *H. tetramera* produced numerous sclerotia on potato glucose agar; no sclerotial bodies developed in the writer's cultures of *H. tetramera* on potato dextrose agar. A study of Bainier's description and drawings shows that *B. spiciferum* is identical with *H. tetramera*. The features of the new genus *Curvularia*, which was established by Boedijn in 1933, and in which *H. tetramera* is now included, are discussed later.

The species under consideration is therefore now known as *Curvularia spicifera* (Bainier) Boedijn (which falls into the "Maculans Gruppe"), the synonyms being *Helminthosporium tetramera* McKinney and *Brachycladium spiciferum* Bainier. The colony growth of two strains of the fungus on potato dextrose agar is illustrated in Plate IX. Concerning the Maculans group, Boedijn writes: "This includes forms showing conidia with three partition walls, and the two middle cells are larger and darker than the end cells. Furthermore, the conidia are here straight or merely asymmetrical. In pure cultures, stromata are never formed. The typical representative of this group is *Spondylocadium maculans* Bancroft."

(2) *Helminthosporium M.* In his investigation of root-rotting fungi, Henry<sup>(8)</sup> isolated several small-spored strains of similar character, to which he applied the name *Helminthosporium M.* The fungus was isolated from wheat seed, millet leaf, and roots of wheat and barley. Pathogenicity tests showed that some strains were rather virulent in producing foot- and root-rot in wheat, others were only weakly parasitic. Henry studied four of the strains, and found that they were of the same general morphological character, the spores being dark olivaceous, usually curved, with a small hilum at the lower end, borne in a similar manner, and germinating usually from both ends. He investigated their specific identity, and his remarks in this connection are of interest:

"The exact identity of these forms is difficult to determine. They apparently may be placed with justification in either of two genera,

namely *Helminthosporium* or *Brachysporium*. If Lindau's suggestion were followed, namely that *Brachysporium* be reserved for species whose spores are not more than twice as long as they are broad, then three of the above strains would belong in the genus *Helminthosporium*, and one in *Brachysporium*. The fungi *Brachysporium trifolii* Kauffman and *Helminthosporium inaequalis* Shear have spores which correspond rather closely in shape and size to the conidia of the forms isolated by the writer. These small-spored cultures were submitted to Dr. Charles Drechsler for identification. He was unable to place them specifically, but preferred to refer them to the genus *Helminthosporium* rather than to *Brachysporium*, and considered that it was impossible without further study to apply either a new or an old binomial to them."

The writer first isolated a small-spored type from wheat roots in New South Wales some years ago, and since it agreed in general morphological characters with *Helminthosporium M* described by Henry, the same designation was adopted for this and other isolates subsequently obtained from diseased roots of oats, barley, *Agrostis* sp., *Bromus inermis*, *Festuca rubra*, *Ischaemum laxum*, *Lolium rigidum* var. *strictum* and *Poa pratensis*. This fungus has also been isolated from material from Victoria and South Australia. Experiments dealing with its pathogenicity and cultural characters have already been described by the writer.<sup>(10)</sup> Certain strains have been shown to be extremely virulent on seedlings of wheat, oats, barley and rye.

A study of the morphology of the fungus when grown on potato dextrose agar at 20° C. (cf. Fig. 3) shows that the spores are borne in clusters on brownish-coloured conidiothores. The conidia are oblong in shape and usually are curved to a greater extent on one side than on the other, presenting a humped appearance. They are not so uniform or symmetrical in shape as those of *H. tetramera*. They are dark brown in colour and predominantly 4-septate, the spore wall being sometimes slightly constricted at the septa, which stand out much more prominently than in the case of *H. tetramera*. A tiny black stipe is to be seen on most conidia. A very striking feature is the darker colour of the large central cell or cells, and the lighter brown of the terminal segments. This was not observed in any isolate of *H. tetramera* studied. In contrast to this species also, the individual protoplasts of spores of *Helminthosporium M* are larger and occupy a greater area in each segment.

The conidia germinate readily in tap water, frequently from each end, and occasionally also from the side of the spore. Conidial material kept for 31 months in test tubes

plugged with cotton wool under laboratory conditions germinated vigorously in hanging drop cultures.

The results of measurement of 100 conidia of each of two monosporous isolates cultured on sterilised wheat heads in test tubes at 20° C. are set out in Table 3. It will be seen

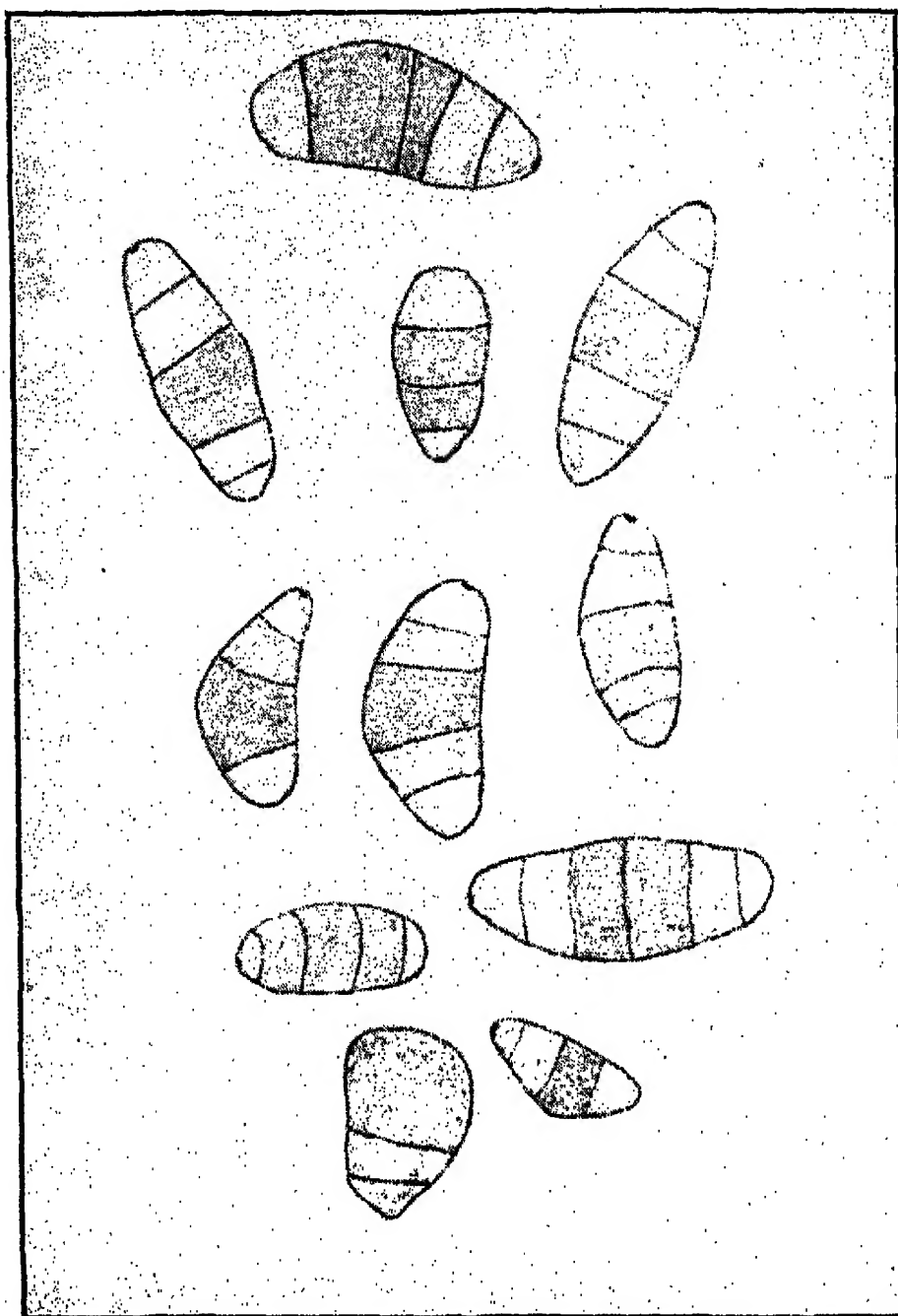


Fig. 3.—Conidia of *Helminthosporium M* (*Curvularia ramosa* (Bainier) Boedijn).  $\times 800$ .

(From cultures on potato dextrose agar at 20° C.)

(Photo by P. R. Maguire.)

TABLE 3.

*Measurements of 100 Conidia of each of two Monosporous Isolates of Helminthosporium M (Curvularia ramosa) Cultured on Sterilised Wheat Heads at 20° C.*

## ISOLATE 1.

| Septation Class. | Frequency % | Range. (Microns.)     | Mean. (Microns.) |
|------------------|-------------|-----------------------|------------------|
| 0                | 1           | —                     | 11.5 × 8.2       |
| 1                | 4           | 11.5-16.5 × 6.6-11.5  | 14.0 × 9.0       |
| 2                | 6           | 14.8-23.1 × 8.2-13.2  | 19.8 × 10.2      |
| 3                | 17          | 23.1-31.3 × 9.9-14.8  | 26.8 × 12.0      |
| 4                | 48          | 29.7-42.9 × 11.5-16.5 | 35.6 × 13.8      |
| 5                | 19          | 26.4-41.2 × 9.9-14.8  | 37.0 × 13.6      |
| 6                | 5           | 36.3-41.2 × 11.5-14.8 | 39.6 × 13.5      |

## ISOLATE 2.

|   |    |                       |             |
|---|----|-----------------------|-------------|
| 1 | 1  | —                     | 21.4 × 14.8 |
| 2 | 3  | 23.1-24.7 × 9.9-11.5  | 23.6 × 10.4 |
| 3 | 10 | 21.4-37.9 × 9.9-14.8  | 28.5 × 12.0 |
| 4 | 50 | 28.0-42.9 × 9.9-16.5  | 35.4 × 13.1 |
| 5 | 30 | 33.0-42.9 × 11.5-16.5 | 38.0 × 14.1 |
| 6 | 6  | 37.9-41.2 × 13.2-16.5 | 40.1 × 14.8 |

Mean length and width of the 100 conidia of isolate 1 : 32.6 × 13.0 microns.

Mean length and width of the 100 conidia of isolate 2 : 35.3 × 13.3 microns.

that the septation class of highest frequency in each case was 4; also that the mean dimensions were 32.6 × 13.0 microns and 35.3 × 13.3 microns, respectively. Henry<sup>(8)</sup> found the mean lengths of conidia of four monosporous strains cultured on sterilised wheat heads to be 26.61, 22.59, 26.7 and 25.2 microns; the mean widths to be 11.77, 11.99, 11.05 and 10.5 microns, respectively; and the mean number of septa to be 3.65, 2.88, 3.76 and 3.69, respectively. Bainier<sup>(1)</sup> observed the dimensions of *Brachycladium ramosum*—which, as indicated below, is a synonym of *Helminthosporium M*—to be 25 to 31 by 11 to 14 microns. ✓

Cultures forwarded to Boedijn have been identified as *Curvularia ramosa* (Bainier) Boedijn, synonymous with

*Brachycladium ramosum* Bainier, which was described in 1908<sup>(1)</sup> from material isolated from "the dead stalks of the common nettle". From a study of Bainier's description and drawings, the writer concludes that *Helminthosporium M* is very similar to *B. ramosum*. The recent critical study of small-spored types by Boedijn<sup>(3)</sup> means that both these forms must now be classified as *Curvularia ramosa*, falling into the "Lunata Gruppe", concerning which Boedijn writes: "The conidia have three partition walls, but only one of the middle cells is larger and darker, and further, the conidia in this case are more or less heavily bent. Most species of this group form cylindrical stromata in pure culture. *Acrothecium lunatum* Wakker is an example." The colony growth on potato dextrose agar of two virulent strains of the fungus isolated by the writer is illustrated in Plate IX.

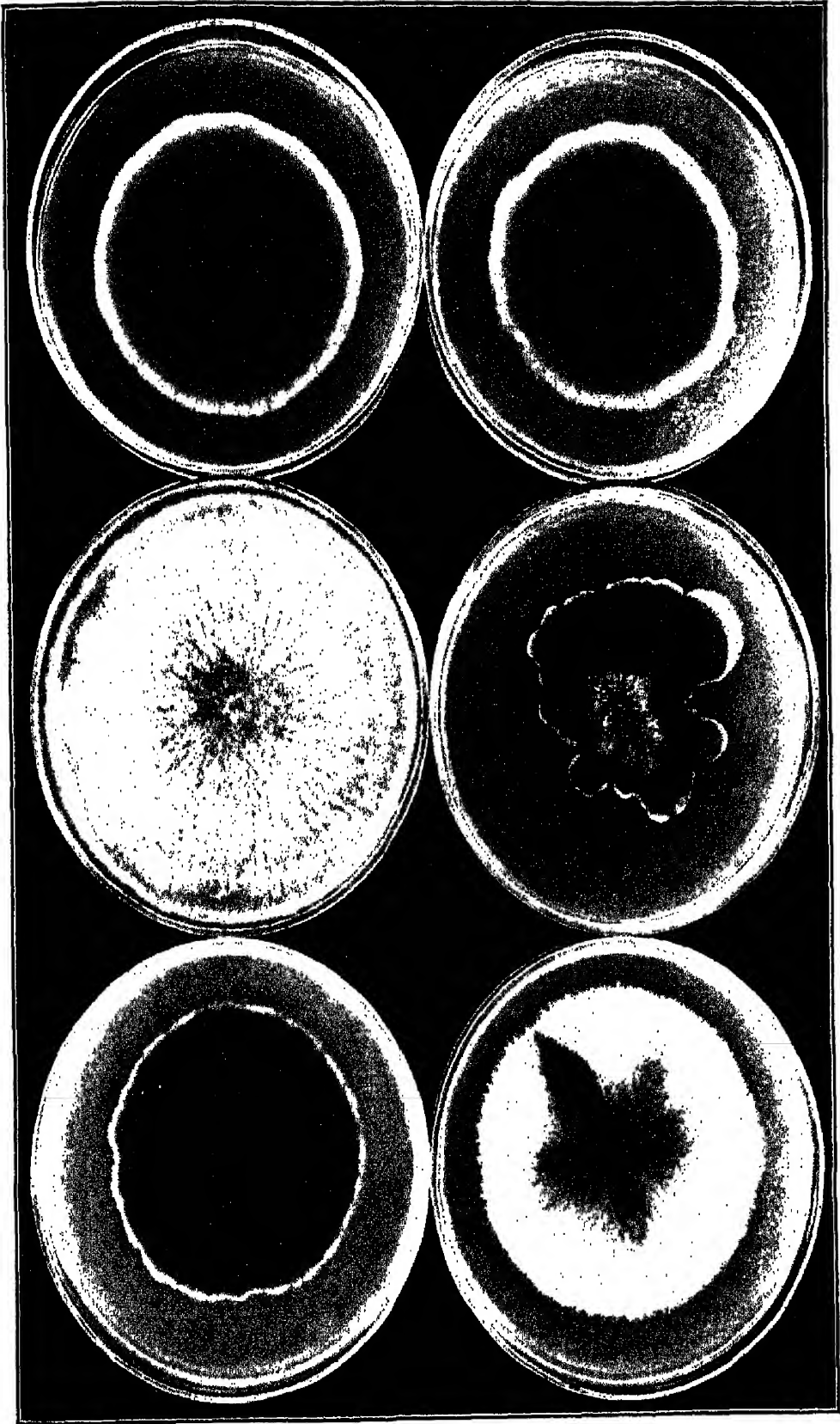
In addition to the Maculans and Lunata groups, Boedijn defines a third section, the "Geniculata Gruppe", in which he includes species with four partition walls in the conidia, and which for the most part form stromata in pure culture. He cites *Helminthosporium geniculatum* Tracy and Earle as a typical representative of the group.

#### SUMMARY.

1. Attention is drawn to the fact that five large-spore species of *Helminthosporium* have been isolated from root-rot-affected wheat by various workers. These are *H. bicolor* Mitra, *H. halodes* Drechs. var. *tritici* Mitra, *H. pedicellatum* Henry, *Helminthosporium N* Henry and *H. sativum* P.K.B. The most important species of this group, however, is *H. sativum*. The writer's studies on the morphology of Australian isolates of *H. sativum* are outlined.

2. The only small-spored species of *Helminthosporium* which appear to have been isolated from root-rot-affected wheat by various workers are *Helminthosporium M* Henry and *H. tetramera* McKinney. The writer's studies on the morphological characters of Australian isolates of each of these species are outlined. It is pointed out that as a result of Boedijn's work, *Helminthosporium M* should now be classified as *Curvularia ramosa* (Bainier) Boedijn, and *H. tetramera* as *Curvularia spicifera* (Bainier) Boedijn.







## EXPLANATION OF PLATE IX.

Colonies of parasitic strains of *Helminthosporium* spp. from foot-rot-affected wheat on potato dextrose agar at 25° C. after six days' growth.

Top: Two virulent strains of *Helminthosporium M* (*Curvularia ramosa*).

Centre: Two virulent strains of *H. sativum*.

Bottom: Two weakly parasitic strains of *H. tetramera* (*Curvularia spicifera*).

Photo by P. R. Maguire.

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## ENERGY DISTRIBUTIONS IN THE SPECTRA OF SOME GASEOUS DISCHARGE TUBES.

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(With Plate X and two text-figures.)

Communicated by PROFESSOR O. U. VONWILLER.

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At the present time, much attention is being given to gaseous discharge tubes for purposes of general illumination. A much greater efficiency, it seems, could be obtained from these than from incandescent lamps, much of the energy of which is emitted in the form of infra-red radiation. The main disadvantage lies in the colour, the spectrum always showing a number of strong lines, and, even though a continuous spectrum can be obtained, the effect is far from that of daylight.

The general suitability of these tubes depends not only on the ratio of the visible light to the energy supplied, but on the energy distribution of the continuous spectrum in the visible region, the intensity of each line in terms of the continuous spectrum in the same neighbourhood, and the eye sensitivity in the various spectral regions. Four discharge tubes, submitted by Neon Signs (Aust.) Ltd., have been tested, and in this paper the photometric methods of examination which have been developed for obtaining the energy distributions are described.

The tubes consisted of three-feet lengths of one-quarter inch internal diameter glass tubing, containing the following mixtures of gases :

- (a) 8 mms. of a mixture of inert gases + Hg. vapour.
- (b) 8 mms. He + Hg vapour.
- (c) 8 mms. Ne + Hg vapour.
- (d) 3 mms. Ar + Hg vapour.

They were run on 4,500 volts A.C. and about 27 mA., thus absorbing about 120 watts. The walls of the tubes were constructed in two sections, the inner section

fluorescing under ultra-violet light, the outer being a covering of opal glass, having a much smaller effect on the quality of the light. A strong continuous spectrum resulted from the fluorescence of the inner section under the stimulation of the ultra-violet light from the Hg discharge. To the eye, the light appeared fairly white, with a bluish tinge of not unpleasant appearance, the colour appreciation being fairly good.

A photographic method of examination was adopted. A wedge-shaped slit was prepared for a Hilger type D<sub>10</sub> constant deviation spectroscopic. This was prepared by attaching a bevelled, straight-edged piece of brass to the movable jaw of the spectrometer slit, the brass edge being slightly inclined to the fixed edge of the slit. The resulting wedge was about 7.5 mms. long, with a maximum width about 0.7 mm., the exact values being of no importance. The image on a photographic plate of the mercury green line  $\lambda$  5461 was examined under a travelling microscope, arranged on two holders at right angles. The width of the wedge-shaped image was measured at different distances from the narrow end, and was found to be proportional to the distance, aberration effects being thus smaller than the experimental error.

It was found necessary to keep the regions of the spectrum being measured near the centre of the field, because marginal parts of the beams emerging from the prism did not all pass through the camera lens. Precautions were taken to minimise the effects of scattered light; different types of plate had to be employed for the blue and red sections of the spectrum, as, with the former in the centre of the field, red light scattered from the side of the camera at grazing incidence affected panchromatic plates. Kodak supersensitive panchromatic and orthochromatic plates were selected as suitable, being free from chemical fogging. The orthochromatic plates were treated with caramel backing to reduce halation, otherwise serious around  $\lambda$  4358. The plates were developed in a special tank in which a plunger was arranged to move close to the surface of the plate, thus ensuring turbulence of the developer and hence reducing effects due to robbing of the developer.

The visible spectrum consisted of mercury lines superimposed on a strong continuous background. On starting the discharge neon lines were prominent in some tubes, but disappeared in a short time, due to readjustment of

potential gradients within the tube. The experimental work fell into two classes :

- (a) The determination of the energy distribution in the continuous spectrum.
- (b) The determination of the energy associated with each line in terms of the energy in the neighbouring continuum.

#### THE CONTINUOUS SPECTRUM.

Using the wedge-shaped slit, the intensity of the spectrum varied across the spectrum from one side to the other. (See Plate X, A.) If, for any wave-length  $\lambda$ , the difference in the effects of the light at  $\lambda \pm \delta\lambda$  is not great, either as regards density of radiation or plate sensitivity, then the intensity of the light anywhere across the spectrum at that wave-length will be proportional to the corresponding width of the slit. If, for convenience, we call the sides of the spectrum corresponding to the narrow and wide ends of the slit the weak intensity and strong intensity sides respectively, then the intensity of the light is proportional to the distance from the weak intensity side.

On the one plate photographs were taken of the spectra of a discharge tube and a standard lamp whose colour temperature was known as a function of the current. (See Plate X, A and B.)

Let

$l_1$  = a distance from the weak intensity side of the spectrum of a discharge tube.

$l_2$  = the corresponding distance on the spectrum of the standard lamp at which the same density is obtained.

$E'_\lambda$  = the energy distribution function for a wave-length  $\lambda$  of light from the standard lamp, falling on the strong intensity side of the spectrum.

$E_\lambda$  = the corresponding function for the discharge tube.

Then

$$E_\lambda = \frac{l_2}{l_1} \times E'_\lambda \dots \dots \dots (1)$$

Hence by a comparison of densities the energy distribution function can be obtained.

The distances  $l_1$ ,  $l_2$  were obtained with a Moll microphotometer. Since the weak intensity side was ill-defined,

but the strong intensity side sharp, the distance  $w-l$  was measured, where  $w$  is the height of the spectrum. The edge of the standard lamp spectrum was focussed on the centre of the thermopile slit, and the photometer handle turned through a certain number of revolutions. The pitch of the screw was 1 mm., and there were 100 teeth on the axle, so, using these as graduations, the displacement of the plate could be read correct to 0.01 mm. The strong intensity side of the discharge tube spectrum was next focussed on the centre of the thermopile, and the distance through which the plate had to be moved for the same galvanometer deflection as before, was obtained. The height  $w$  of the spectrum was measured with the travelling microscope, using the mercury lines, these retaining a constant density up to the narrow end of the slit. The height was plotted against the wave-length. The distances  $l_1, l_2$  could then be obtained.

For the completion of formula (1), the values of  $E'\lambda$  were obtained from graphs of Planck's Law.\*

Three plates were required for the different sections of the spectra. The density in the red end of the spectrum was so much greater than that in the green and blue that a considerably shorter exposure was required for measurements on the former than for the latter. Two panchromatic plates were used, and an orthochromatic plate was used for the violet. Overlapping sections of each plate were correlated, and the whole energy distribution in the continuous spectrum was thus mapped out. The distributions for each tube are given in Fig. 1. For comparison purposes, the energy distribution for a black body at 5,000° A. is also given.

#### THE INTENSITY OF THE LINES.

For a sufficiently narrow slit a spectral line has a definite shape, but the energy in the line is distributed over quite a small range of wave-lengths, the distribution function falling rapidly to zero away from the centre of the line. Increasing the width of the slit is equivalent to summing the energy in a region of wave-lengths equal to the widths of the slit image. Hence, for a sufficiently wide slit, neglecting the continuous background, the intensity of the light will be constant throughout the image, and will be equal to the integrated energy in the line. Thus the line should be of constant density, except near the sloping

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\* Miscellaneous Publications of the Bureau of Standards, No. 56.

edges. However, owing to the superimposed continuous background, to this constant density must be added a component which increases from the narrow to the wide end of the wedge-shaped line; the density would thus be expected to increase from the narrow to the wide end. Except in the case of the weak line  $\lambda 4916$ , however, the intensity of the line is so great compared with that due

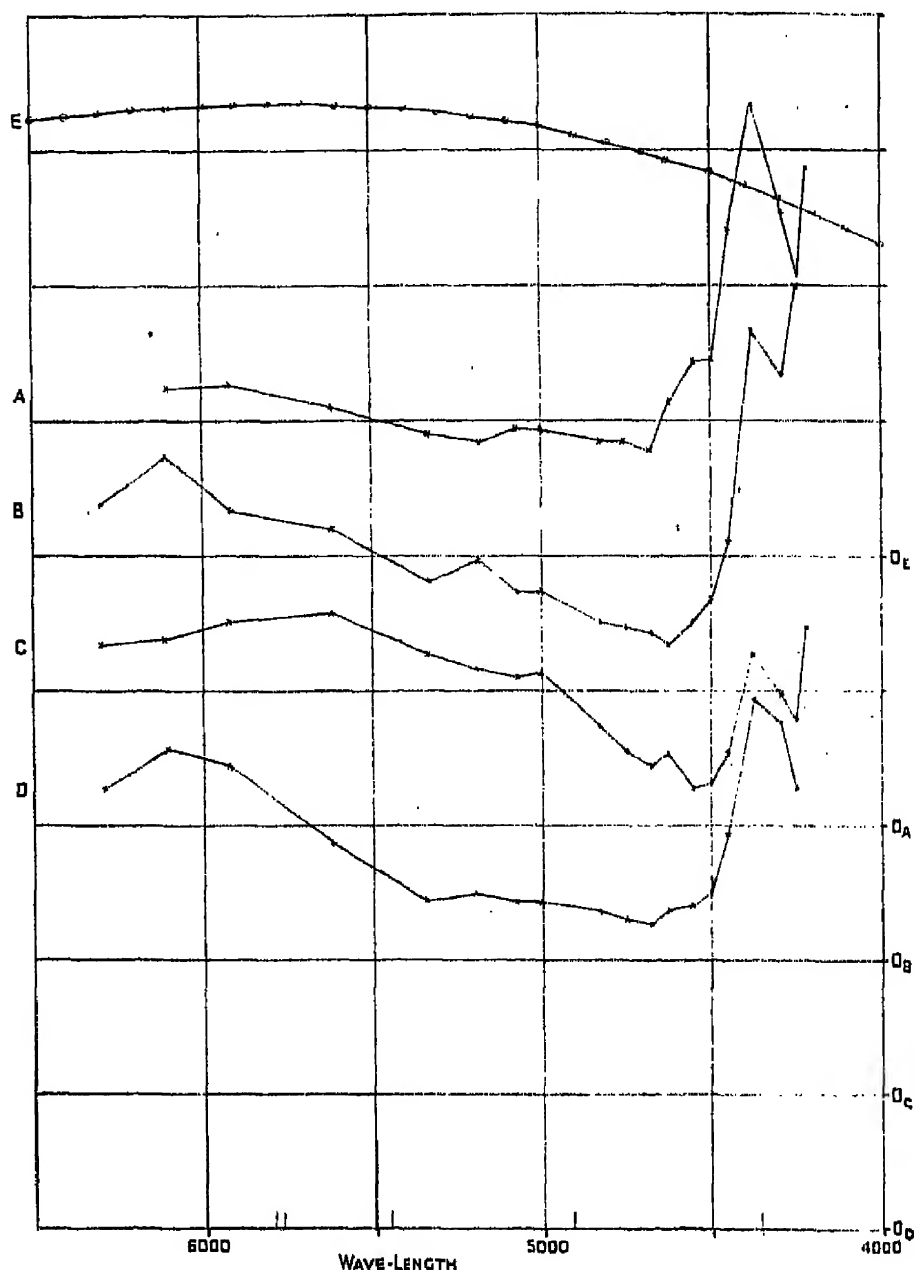


Fig. 1.—Energy distribution curves. The letters A, B, C, D, E refer to the curves for tubes A, B, C, D and a black body at  $5,000^{\circ}\text{A}$ . respectively. For clearness the curves have been separated, the origins being denoted by  $0_A$ ,  $0_B$ ,  $0_C$ ,  $0_D$ ,  $0_E$ . The positions of the lines are indicated on the  $\lambda$  axis.



to the continuous spectrum that this effect is not noticeable, and, on the contrary, robbing of the developer causes a slightly weaker deposit than expected for a section of the plate surrounded by wide patches of dense deposits.

In order to make a comparison between the intensity of the line and the surrounding continuous spectrum, it was necessary to reduce the intensity of the line by placing a screen in front of the spectroscopy slit, photographs of the unscreened and screened spectra being recorded on the one plate.

The screen was prepared by exposing four sections of a lantern plate for different times to a 20 watt lamp at a distance of about 12 feet; these we may denote, in order of increasing density, by  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$ . The calibration of the screen in different spectral regions was carried out, using the wedge-shaped slit. It was found that, were the spectra of the light passing through the two screens photographed separately, owing to the large difference in intensity, there would be a considerably larger amount of scattered light in one case than in the other. To overcome this the adjoining sections of two screens, say  $\alpha$  and  $\beta$ , were placed over the slit together, the denser screen  $\beta$  being placed over the wider portion of the slit, and the less dense screen  $\alpha$  covering the narrow end (see Plate X, C). Scattered light, which is assumed proportional to the intensity of incident light, is reduced, and, since it has no directional effect, falls evenly over both halves of the spectrum. Thus the effects on the plate of beams of initially equal intensities will be identical. The distances  $l_\alpha$  and  $l_\beta$  from the weak intensity side of the spectrum at which equal densities were obtained were measured,  $l_\alpha$  and  $l_\beta$  corresponding to screens  $\alpha$  and  $\beta$  respectively. Relative intensities of the light transmitted by each section of the screen were thus obtained; in this way a complete calibration of the screen was carried out for all the wavelengths required.

A series of photographs was now taken on the one plate of the spectrum of the discharge tube, the light passing through different screens before entering the slit, the ratio of the more to the less intense beam for a given wave-length being  $C$ . For the measurements of the intensities, the plate was placed in the photometer carriage, so that the lines were parallel to the direction of travel. The thermopile was removed from its normal stand and clamped in a horizontal position so that the slit was parallel

to the lines; so that for the narrower lines (such as the non-overlapping portions of the yellow doublet) light from outside might not fall on the thermopile.

The distances  $l_+$  and  $l_-$  respectively on the long and short wave sides of the line at which the density of the continuum was the same in the lightly screened spectrum, as was the line in the heavily screened spectrum, were then measured.

Let

$A$  = the dispersion of the instrument in Ångström units/mm.

$S$  = the width of the wide end of the slit image for monochromatic light.

$w$  = the total height of the spectrum.

If the energy distribution were uniform, the dispersion the same, and the plate uniformly sensitive at wavelengths corresponding to  $l_+$  and  $l_-$ , then

$$l_+ = l_- = l, \text{ say,}$$

and the energy in the line would be

$$A \times C \times \frac{l}{w} \times S \times E \dots\dots\dots (2)$$

where  $E$  is the energy in one Ångström unit of the continuous spectrum. Since these assumptions are not quite true, the value of  $l$  used is

$$l = \frac{l_+ + l_-}{2}.$$

Different combinations of screens were used to give results for different lines. By the application of the above formula, the ratio of the energy in the line to the energy in one Ångström of the continuous spectrum,

$$A \times C \times \frac{l}{w} \times S$$

was obtained. The results are given in Table 1, where the figures indicate this ratio.

TABLE 1.

| $\lambda$ | Tube A. | Tube B. | Tube C. | Tube D. |
|-----------|---------|---------|---------|---------|
| 5,791     | 210     | 300     | 160     | 175     |
| 5,770     | 195     | 295     | 150     | 165     |
| 5,461     | 850     | 910     | 1,000   | 800     |
| 4,916     | 11      | 17      | 28      | 8       |
| 4,358     | 1,400   | 935     | 850     | 940     |

It is estimated that the results are correct to within ten per cent.

### DISCUSSION OF RESULTS.

The general features of the energy distribution in the continua are the same in each of the tubes, which is as expected, the origin (excitation of fluorescence by ultra-violet mercury lines) being the same for each. Variations may be due to experimental errors and to variations in the relative intensities of the exciting lines. It is noticed that, with the exception of the visually unimportant violet regions, the agreement with the black-body curve for  $5,000^{\circ}$  A. is very good.

The ratio of the intensities of the green ( $\lambda$  5461) and blue ( $\lambda$  4358) lines is roughly constant (except in the case of tube A), which is also to be expected as they originate in the same atomic state. The ratio of the lines in the yellow doublet is also constant.

### LUMINOSITY.

The luminosities of the tubes in the different spectral regions were obtained by multiplying the energy by the corresponding visibility. The results given by Gibson and Tyndall\* for the visibility have been used. The luminosity distributions of the continuous spectra are given in Fig. 2. For comparison purposes, the luminosity curves for black bodies at  $6,000^{\circ}$  A. and  $3,000^{\circ}$  A., corresponding to sun light and bright electric lamps are also given. It is seen that the luminosity of the continua corresponds to that of the black bodies at about  $5,000^{\circ}$  A., and is thus favourable.

The luminosities of the lines were also calculated and the total luminosity of the lines compared with that of the continuous spectrum. Results are given in Table 2.

TABLE 2.

|                  | Tube A. | Tube B. | Tube C. | Tube D. |
|------------------|---------|---------|---------|---------|
| Line .. ..       | 110     | 96      | 89      | 78      |
| Continuous .. .. | 100     | 100     | 100     | 100     |

\* Scientific Papers of the Bureau of Standards, 1923, 19, 131.

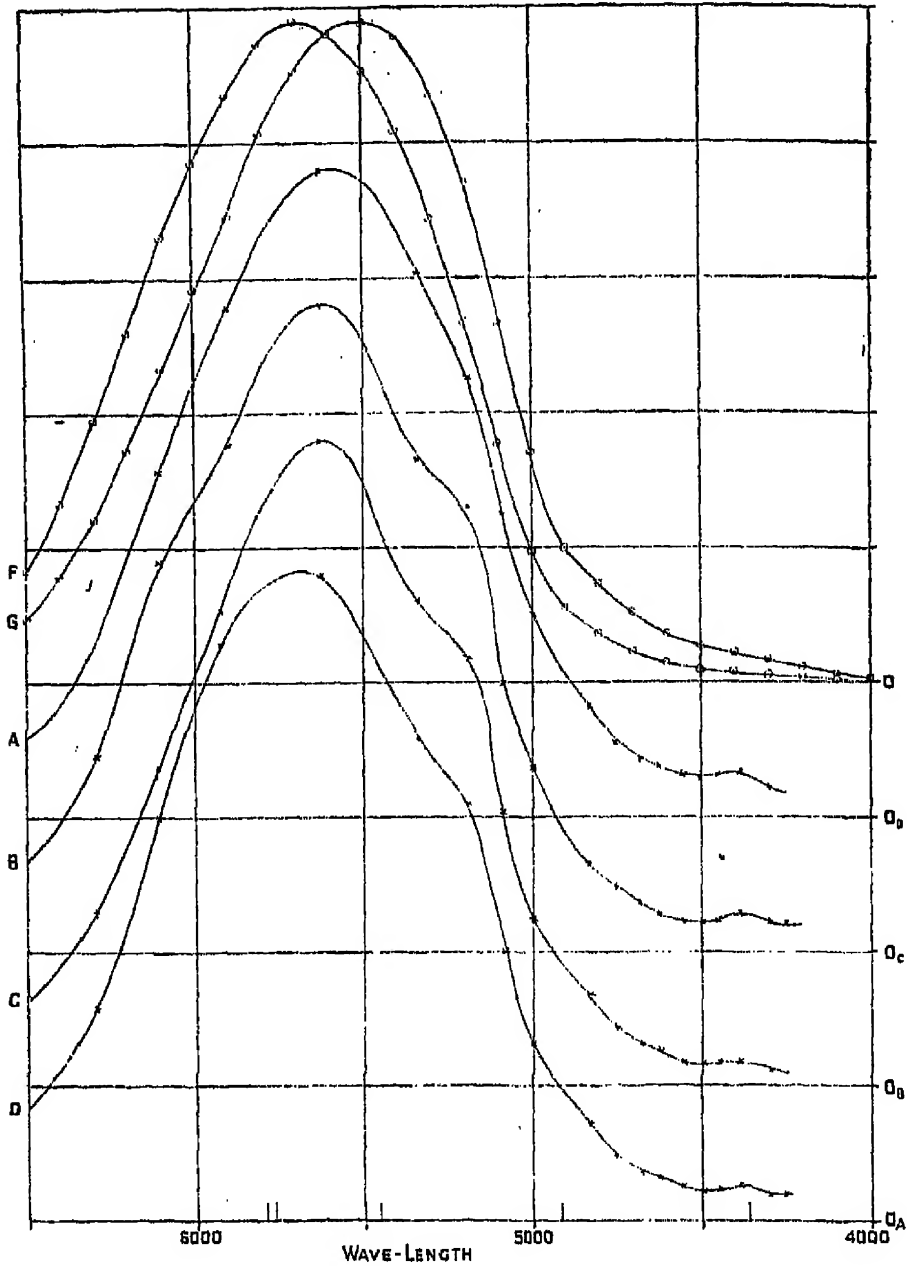
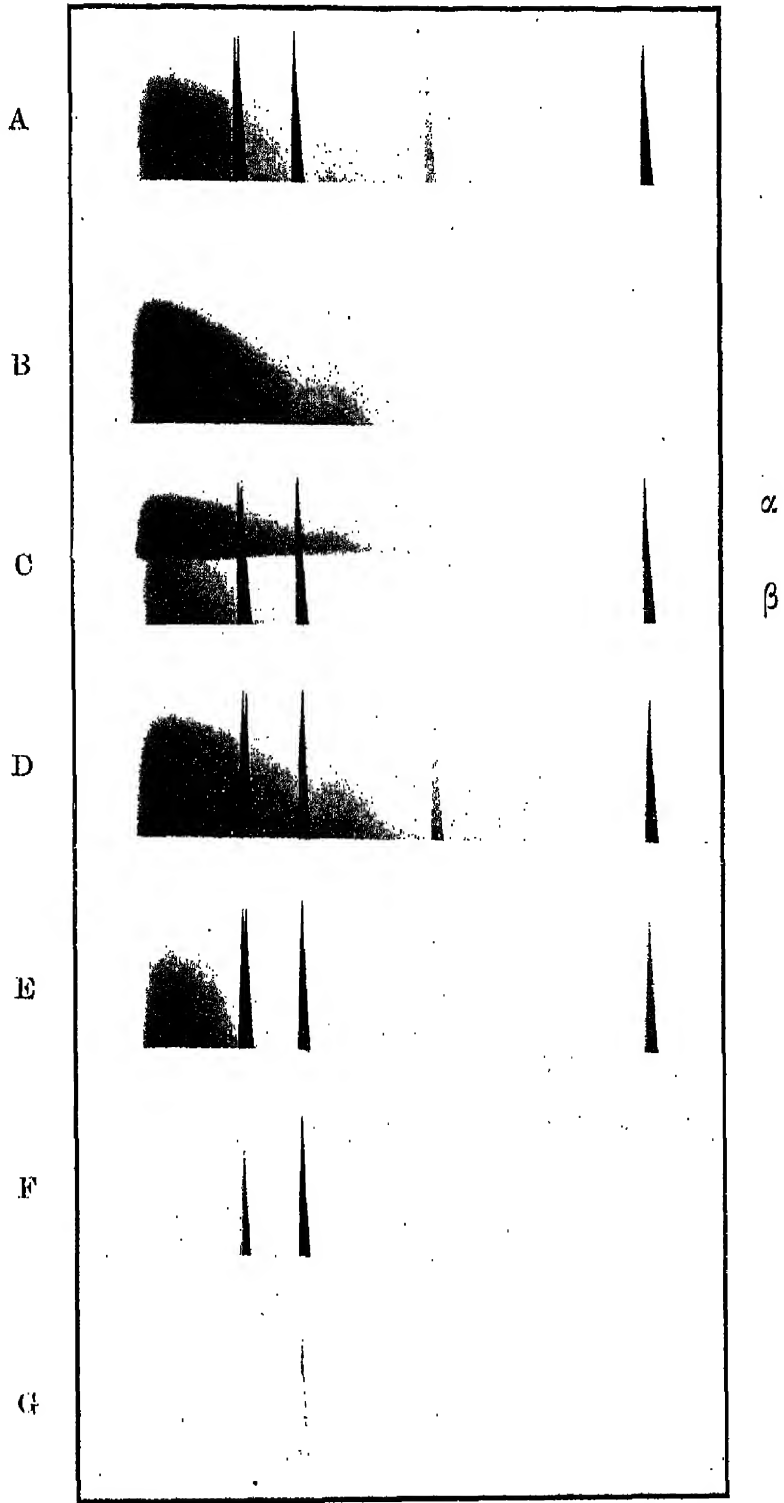


Fig. 2.—Luminosity distribution curves. The letters A, B, C, D, F, G refer to the tubes A, B, C, D, and black bodies at  $3,000^{\circ}$  and  $6,000^{\circ}$  respectively, the origins being again separated except in the case of the two black bodies. The units have been arbitrarily chosen to make all the values equal at  $\lambda 5600$ .

From this it appears that the luminosity is about evenly divided between the continuous and line spectra.

#### ACKNOWLEDGMENTS.

The Moll microphotometer used during these experiments was purchased from the funds of the Cancer Research Committee.





I wish to thank Professor Vonwiller for the suggestions and advice that he has offered throughout this work.

#### EXPLANATION OF PLATE X.

A and B are spectra of a discharge tube and black body respectively. Note the uniform intensity of the lines as compared with the variable intensity of the continuous spectrum; also the sharp definition on the strong intensity side.

C shows the spectrum obtained for calibrating the screens.

D to G are spectra of light passing through screens of increasing density.  $\lambda$  5461, for example (the heavy line in G), can be directly compared with the continuum in D.

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PROBABLE LATE SILURIAN AGE OF  
SERPENTINE, CONDOBOLIN-TRUNDLE  
DISTRICT, NEW SOUTH WALES.\*

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Many of the serpentine occurrences in New South Wales are briefly described in W. R. Browne's Presidential Address to the Linnean Society, 1929.<sup>(1)</sup> He pointed out that apart from W. N. Benson's detailed study of the Great Serpentine Belt, little attention had been given to these rocks. Regarding the serpentines of the south-western part of the State, he writes (p. xxvii): "Nothing appears to be known as to the geological age of these rocks. They are associated with unfossiliferous slaty rocks, evidently of great age and surmised to be Silurian." He tentatively assigned them to a late Middle Devonian or Kanimbla intrusive epoch, but now considers they are more likely to have been of Silurian age (verbal communication).

During recent field work in the Condobolin-Trundle district evidence was found supporting this opinion. Condobolin is 240 miles in a direction a little north of west from Sydney.

In this district there is a great development of dominantly argillaceous rocks. These rocks are commonly slates, folded and crushed in varying degree. Some of the more altered types are schistose. Fossils are not common in these beds, but it is significant that at three rather widely separated localities where these have been found they suggest an Upper Silurian age for the less altered beds at least.

In the early stages of the geological survey of this area consideration was given to the possibility of the more altered types representing older rocks exposed on plunging folds, but later work suggested that the rocks represent

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\* Published with the permission of the Under Secretary for Mines.



the deposits of one geological period traversed by zones of shearing of different intensity, rather than rocks of different geological periods. The fortunate discovery near Melrose of two specimens of *Tryplasma princeps* in a crushed limestone interbedded with some of the most altered rocks of the district, tends to confirm this view.

A further line of evidence tending to support the conclusion that most, if not all, of these phyllitic and slaty rocks are Silurian is that they differ markedly from the known Ordovician in adjacent areas. Recently Mr. Booker and myself discovered two new outcrops of Upper Ordovician rocks, one near Weeja, 36 miles S.S.W. from Condobolin, and one on the eastern slope of McGregor Trig. Station, 16 miles S.W. from Condobolin. These no doubt represent the northward continuation of the Yalgogrin Ordovician beds described by L. F. Harper.<sup>(2)</sup> The important point about these outcrops is that their lithology instantly suggests their Ordovician age to the observer, an impression confirmed by the finding of graptolites at Weeja. The strata are thinly bedded bluish-black slates interbedded with thick white quartzites, the latter much fractured. Although careful search has been made, these lithological types could not be found on the north side of the Lachlan River, where the typical Silurian slates and phyllites are so well developed.

The slate series, as exposed in the Condobolin district, is undoubtedly continuous with the Nymagee beds, and these in turn Mr. A. C. Lloyd considers<sup>(3)</sup> may be correlated with the Canbelego and Cobar Series of E. C. Andrews.<sup>(4) (5)</sup> It is, therefore, proposed to refer the whole of the slaty rocks of the Condobolin-Trundle district to the Cobar Series, which is thus regarded as Silurian.

This conclusion on the evidence now available seems inescapable. It may be noted that it agrees with the original conclusion of E. C. Andrews,<sup>(4)</sup> but differs from those expressed by him later.<sup>(5) (6)</sup> The writer considers that too much emphasis has been placed on the value of degree of metamorphism as indicating difference in age in these areas, and that unconformity between the known fossiliferous Silurian and the crushed slates and phyllites cannot be proved. The view that these rocks are pre-Silurian gained support also from the failure to find fossils in the interbedded limestones, a support which is now largely removed at least so far as the Condobolin district is concerned.

The Cobar Series is overlain unconformably by a considerable thickness of Devonian sediments. These include agglomerate, conglomerate, quartzite, sandstone, green shaly sandstones, red shales and limestone. The upper part of the sequence is Upper Devonian (Lambian), as the fossil evidence proves.<sup>(7) (8) (9)</sup> A representative collection has been made from limestones and sandstones in the lower part of the section, but has not yet been described. The late W. S. Dun considered that the Middle Devonian might be represented in the western sequence.<sup>(7) (8)</sup> The basal beds not only rest with marked angular unconformity on an uneven basement of the Cobar Series, but in places contain large blocks of slate with vein quartz. It is clear, therefore, that the Cobar Series suffered marked deformation, mineralisation and erosion before the deposition of the Devonian. Associated with the late Silurian diastrophism were injections of porphyry and granite.

Ultra-basic rocks are not uncommon in the district. The best known is the amphibolite near Fifield, with which are associated some of the most important magnesite deposits in New South Wales.<sup>(10)</sup> The magnesite deposits referred to by Mr. Morrison one and a half miles south to 13 miles S.W. from Gobondery also occur in ultra-basic rocks.<sup>(10)</sup> (Mr. Whitworth informs me that he has observed serpentine in one of the magnesite quarries near Fifield.) L. F. Harper and E. J. Kenny record "granite amphibolite and serpentine intruding sediments at Tullamore and Fifield".<sup>(11)</sup> Early this year serpentine (with magnesite) was noted near Collerina, 25 miles N.W. from Tottenham. All these occurrences are in strata almost certainly not older than the Cobar Series.

My attention was drawn recently to a magnesite deposit near Mineral Hall (42 miles northerly from Condobolin) by Mr. T. Pearce. The magnesite occurs in chloritic schists, and it is with rocks similar to these that the limestone is associated in which the *Tryplasma princeps* was found.

Three and a half miles east of Mineral Hill, and five and a half miles north-east of the magnesite deposit discovered by Mr. Pearce, are some so-called alluvial workings known locally as "Miller's Paddock". The workings are not in alluvial deposits, but in deeply weathered Devonian conglomerates. Amongst the débris from one of the shafts pebbles of serpentine and magnesite were found.

The age of the serpentine is thus fixed within a fairly restricted range from Upper Silurian to possibly Middle Devonian. The geological history of the region suggests that the serpentine was injected during the late Silurian diastrophism.

It seems reasonable tentatively to assign other serpentine occurrences in the southern and western parts of New South Wales (Gundagai-Wallendbeen, Lucknow-Byng, Rockley) to the same diastrophic epoch.

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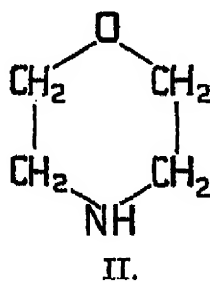
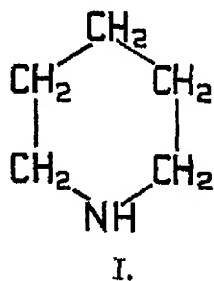
MORPHOLINE AS A REAGENT FOR MOBILE  
HALOGEN ATOMS AND NITRO GROUPS.By RITA H. HARRADENCE  
and FRANCIS LIONS, B.Sc., Ph.D.

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*(Manuscript received, November 20, 1936. Read, December 2, 1936.)*

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Le Fèvre and Turner (*J.C.S.*, 1927, 1113) have shown that piperidine (I) is much superior to alcoholic ammonia, aromatic amines, hydrazines, alkyl oxides, etc., as a reagent for reactive halogen atoms, the advantages contributing to the superiority being "(1) the substituted phenyl piperidines are, as a rule, highly crystalline; (2) piperidine reacts much more readily than most bases with mobile halogen atoms; and (3) the interaction of piperidine with halogen compounds is generally characterised by the absence of by-products". Recent developments in technical chemistry have rendered another secondary heterocyclic base, morpholine (II), rather readily accessible, and in view of its relative cheapness compared with piperidine, and its already established power of yielding



highly crystalline derivatives (cf. H. A. Bruson, U.S. Patents 2,040,039 and 2,040,040; *Chemical Abstracts*, 1936, 30, 4177), it was considered desirable to test its value as a reagent for mobile halogen atoms or nitro groups in various organic compounds.

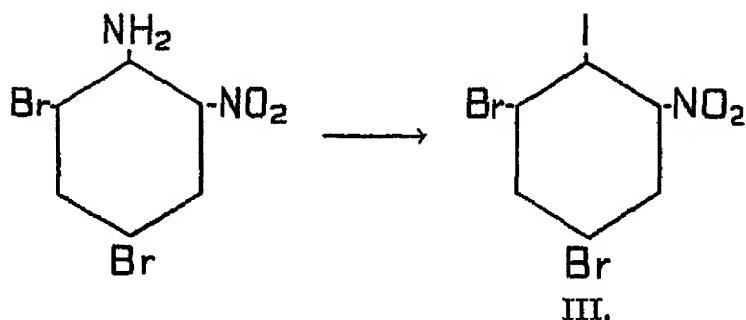
It was found in comparative experiments that, whilst morpholine does replace such activated atoms and groups, it does not react as readily as does piperidine. At the same time it shares with piperidine the advantage of not

yielding by-products in such replacement reactions, and the substituted phenyl morpholines are highly crystalline and much more readily purified than the corresponding phenyl piperidines. The melting points of the former are, in general, higher than the corresponding members of the latter. Thus, by the action of piperidine on 3 : 4-dichloronitrobenzene Le Fèvre and Turner (*loc. cit.*) obtained 2-chloro-4-nitro-phenyl piperidine as an oil which required special treatment to induce crystallisation and melted at 47°-48°. The corresponding 2-chloro-4-nitrophenyl morpholine is obtained crystalline without any difficulty and melts at 127°. The slower rate of reaction of morpholine compared with piperidine may perhaps be turned to account in the study of the reactivity of halogen atoms in compounds which react too rapidly with piperidine.

The general method of procedure, described in the experimental section, was to reflux the aromatic halogen or nitro compound with about two or three times the calculated quantity of morpholine for about three hours, and then to treat the reaction mixture with an excess of cold very dilute hydrochloric acid. The substituted phenyl morpholine usually crystallised and could be readily purified. By this method 2-nitrochlorobenzene, 2-nitrobromobenzene and 2-nitroiodobenzene all yield 2-nitrophenyl morpholine; 4-nitrochlorobenzene gives 4-nitrophenyl morpholine; 2 : 4-dinitrochlorobenzene reacts very easily to give the 2 : 4-dinitrophenyl morpholine melting at 118°-119° which was previously obtained by Marckwald and Chain by nitration of N-phenyl morpholine (*D.R.P.*, 119,785). Some difficulty was experienced in the purification of the 2-nitro-6-methyl phenyl morpholine from 2-iodo-3-nitrotoluene, and it is worthy of comment that the reactions involving compounds with reactive iodine atoms usually led to very dark coloured mixtures.

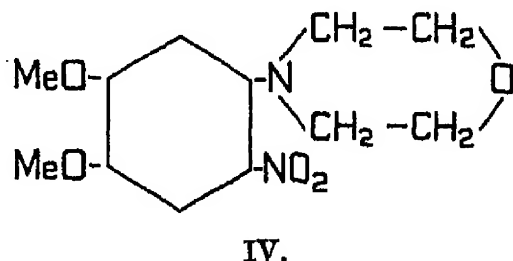
As was to be expected, treatment of 2 : 5-dichloronitrobenzene and 3 : 4-dichloronitrobenzene leads to replacement of only one chlorine atom, the former substance yielding 2-nitro-4-chlorophenyl morpholine and the latter 2-chloro-4-nitrophenyl morpholine. Similarly, 4 : 6-dibromo-2-nitroiodobenzene (III) which can be obtained from dibromo-o-nitraniline *via* the diazo reaction, reacts to form 4 : 6-dibromo-2-nitrophenyl morpholine, neither of the bromine atoms being replaced.

The observation of Le Fèvre and Turner that "introduction of a third group, e.g. carboxyl or carbethoxyl,



which by itself has feeble activating effect, produces a very marked exaltation of reactivity when its effect supports that of the nitro group" has been confirmed with morpholine. Thus, whilst 2:4-dinitro-chlorobenzene reacts easily with morpholine on warming, 2-chloro-3:5-dinitrobenzoic acid and its methyl ester react vigorously even in the cold. *p*-Chlorobenzoic acid does not react at all with boiling morpholine, even after two days' refluxing.

Finally, it was observed that 4:5-dinitroveratrole reacts easily with hot morpholine to yield 2-nitro-4:5-dimethoxy phenyl morpholine (IV), which can also be



readily obtained from 4-bromo-5-nitroveratrole and morpholine (cf. Parijs, *Rec. Trav. Chim.*, 1930, 49, 45). In the same way 4:5-dinitrocatechol di-*n*-butyl ether reacts with morpholine to form 2-nitro-4:5-di-*n*-butyloxy phenyl morpholine.

#### EXPERIMENTAL.

*Preparation of Substituted Phenyl Morpholines.*—In each instance the halogenonitro compound, or dinitro compound was refluxed with two or three times the theoretical quantity of morpholine for two or three hours; usually the reaction appeared to be complete long before this. Reaction was usually accompanied by the appearance of a red colour, which was noticeable even in the cold with the more reactive compounds. When compounds with

reactive iodine atoms were used the mixtures became very dark in colour and the products were discoloured. On cooling, the reaction mixture usually set to a crystalline mass of the product and morpholine hydrohalide, or to a crystalline magma of the latter. In every instance the product was treated with excess of cold very dilute hydrochloric acid and when the insoluble phenyl morpholine crystallised it was filtered off, washed and recrystallised from alcohol or aqueous alcohol to constant melting point.

*2-Nitrophenyl morpholine* (2.5 grams) was obtained from 2-nitro-chlorobenzene (2 grams) and morpholine (2.6 grams); or from 2-nitrobromobenzene, or 2-nitroiodobenzene, and morpholine. Orange needles melting at 42°.

Found : C=57.7, H=5.7% ; calculated for  $C_{10}H_{12}O_3N_2$ , C=57.7, H=5.8%.

*4-Nitrophenyl morpholine* (2.3 grams) was obtained from 4-nitrochlorobenzene (2 grams) and morpholine (2.6 grams). Flat orange-yellow plates melting at 149°-150°.

Found : C=57.6, H=5.7% ; calculated for  $C_{10}H_{12}O_3N_2$ , C=57.7, H=5.8%.

*2 : 4-Dinitrophenyl morpholine* (2.4 grams) from 2 : 4-dinitrochlorobenzene (2 grams) and morpholine (2 grams). Orange-yellow needles melting at 118°-119°.

Found : C=47.4, H=4.4% ; calculated for  $C_{10}H_{11}O_5N_3$ , C=47.4, H=4.4%.

*2-Nitro-4-chlorophenyl morpholine* (2 grams) from 2 : 5-dichloronitrobenzene (2 grams) and morpholine (2 grams). Flat orange platelets melting at 47°.

Found : C=49.0, H=4.2% ; calculated for  $C_{10}H_{11}O_3N_2Cl$ , C=49.5, H=4.5%.

*2-Chloro-4-nitrophenyl morpholine* (3.8 grams) from 3 : 4-dichloronitrobenzene (3 grams) and morpholine (3 grams). Lemon-yellow plates melting at 127°.

Found : C=49.2, H=4.4% ; calculated for  $C_{10}H_{11}O_3N_2Cl$ , C=49.5, H=4.5%.

*4 : 6 - Dibromo - 2 - nitroiodobenzene.* 4 : 6 - Dibromo - 2 - nitraniline (150 grams) was dissolved in concentrated sulphuric acid (450 cc.) and the solution cooled to 0° C. Finely powdered sodium nitrite (90 grams;  $2\frac{1}{2}$  mols.) was slowly added to the well cooled vigorously stirred solution. Towards the end of the addition the stirring had to be carried out by hand, owing to the mixture becoming very stiff. Finally, the mixture was poured on to crushed ice. After thoroughly mixing some unchanged amine was recovered by filtration and the clear pale yellow

solution of the diazonium compound was treated with a cold concentrated solution of potassium iodide (400 grams ; 5 mols.). A vigorous reaction ensued and much gas, including nitrous fumes, was evolved. At the same time an orange precipitate was formed. Eventually the liquid was heated on the water-bath for thirty minutes. The orange solid melted during this treatment and became dark brown-red in colour, but it resolidified on cooling ; yield, 160 grams. This crude product contained iodine which was removed by melting the solid in hot dilute sodium bisulphite solution. The orange-yellow solid obtained after this treatment was recrystallised from ethyl alcohol, in which it is quite soluble in the hot, but only moderately so in the cold. It was thus obtained in lemon-yellow needles melting at  $82^{\circ}$ .

Found :  $C=17.4$ ,  $H=0.8\%$ ,  $N=3.4\%$  ; calculated for  $C_6H_2O_2NBr_2I$ ,  $C=17.7$ ,  $H=0.5$ ,  $N=3.4\%$ .

*4:6-Dibromo-2-nitrophenyl piperidine.* 2:4-Dibromo-6-nitroiodobenzene (5 grams) was dissolved in piperidine (15 cc.) and the solution boiled for an hour. It rapidly became orange in colour and small crystals of piperidine hydroiodide separated. The hot liquid was eventually poured into water and the orange oil which separated was induced to crystallise after standing for some time. Recrystallised from alcohol, it was obtained in magnificent orange prisms melting at  $73^{\circ}$ .

Found :  $C=36.0$ ,  $H=3.0$ ,  $N=7.5\%$  ; calculated for  $C_{11}H_{12}O_2N_2Br_2$ ,  $C=36.5$ ,  $H=3.3$ ,  $N=7.7\%$ .

*4:6-Dibromo-2-nitrophenyl morpholine* (1.8 grams) from 4:6-dibromo-2-nitroiodobenzene (2 grams) and morpholine (2 grams) in orange-yellow prisms melting at  $105^{\circ}$ .

Found :  $C=32.9$ ,  $H=2.9\%$  ; calculated for  $C_{10}H_{10}O_3N_2Br_2$ ,  $C=32.8$ ,  $H=2.7\%$ .

*2-Nitro-6-methylphenyl morpholine.* Difficulty was experienced in obtaining this substance. Eventually it was obtained in poor yield (0.2 gram) by refluxing 2-iodo-3-nitrobenzene (3 grams) with morpholine (3 grams) in alcohol (10 cc.) for five hours. Three recrystallisations from alcohol gave lemon-yellow prisms melting at  $135^{\circ}$ - $136^{\circ}$ .

Found :  $N=12.2\%$  (micro) ; calculated for  $C_{11}H_{14}O_3N_2$ ,  $N=12.6\%$ .

*3:5-Dinitro-2-morpholinobenzoic acid.* 3:5-Dinitro-2-chlorobenzoic acid (2.5 grams) and morpholine (4 grams)



reacted vigorously when mixed in the cold, a red colour appearing at once and heat being evolved. After heating for one hour and treatment with dilute hydrochloric acid, the product crystallised and was recrystallised from alcohol. Short yellow prisms melting with decomposition at  $203^{\circ}$ - $204^{\circ}$ , with previous darkening and softening.

Found: C=44.8, H=4.1%; calculated for  $C_{11}H_{11}O_7N_3$ , C=44.5, H=3.7%.

*Methyl 3:5-dinitro-2-morpholino benzoate.* Methyl 3:5-dinitro-2-chlorobenzoate (2.6 grams) and morpholine (3 grams) were carefully mixed with cooling, and finally heated for one hour. After treatment with dilute hydrochloric acid the product (3 grams) solidified and was recrystallised four times from alcohol. Yellow prisms, melting at  $106^{\circ}$ . Recrystallisation of this substance was difficult.

Found: C=46.5, H=4.4%; calculated for  $C_{12}H_{13}O_7N_3$ , C=46.3, H=4.2%.

*2-Nitro-4:5-dimethoxyphenyl morpholine* (2.6 grams) from 4-bromo-5-nitroveratrole (3 grams) and morpholine (3 grams). Recrystallised four times, it formed bright orange-yellow prisms melting at  $115^{\circ}$ - $116^{\circ}$ .

Found: C=53.7, H=6.3%; calculated for  $C_{12}H_{16}O_5N_2$ , C=53.7, H=6.0%.

The same substance is also obtained by heating together 4:5-dinitroveratrole (2 grams) and morpholine (2 grams).

*2-Nitro-4:5-di-n-butyloxy phenyl morpholine* (1.6 grams) from 4:5-dinitrocatechol di-n-butyl ether (1.5 grams) and morpholine (1.5 grams). Bright yellow matted needles, melting at  $75^{\circ}$ - $76^{\circ}$ .

Found: C=61.8, H=8.1%; calculated for  $C_{18}H_{28}O_5N_2$ , C=61.4, H=8.0%.

#### COMPARISON OF THE REACTIVITIES OF PIPERIDINE AND MORPHOLINE.

Brewin and Turner (*J.C.S.*, 1928, 332) have described the use of piperidine in determining the relative degrees of activation of chlorine, bromine and iodine atoms by nitro-groups, and Sandin and Liskear (*Journ. Amer. Chem. Soc.*, 1935, 57, 1304) used the same reagent with a modified procedure to determine the combined effect of a para nitro group and one or more ortho halogen atoms on the reactivity of an aryl halide. The method of these latter authors was adopted for the comparison between morpholine and piperidine. The halogenated nitrobenzene (0.003685

mol.) was allowed to react in an all-glass reflux apparatus with piperidine or morpholine (0.1088 mol.) in benzene (20 cc.). The piperidine used boiled at 105.5-106.5°/760 mm. and the morpholine at 128°/760 mm.; the benzene was thiophene free and distilled from sodium. Parallel experiments, one using piperidine and the other morpholine, were carried out side by side, heating for the same length of time and in the same oil-bath, so as to minimise accidental variations of temperature, etc. At the conclusion of the heating, the halide ion was extracted quantitatively with water and determined volumetrically. The results obtained are tabulated.

| Substance.              | Temperature of Bath. | Time of Heating. | Per cent. Halogen Removed. |             |
|-------------------------|----------------------|------------------|----------------------------|-------------|
|                         |                      |                  | Piperidine.                | Morpholine. |
| 2-Nitrobromobenzene ..  | Approx. 110°         | Hours. 1.75      | 95.7                       | 53.3        |
|                         | 85°                  | 1                | 74                         | 21          |
| 4-Nitrochlorobenzene .. | 85°                  | 7                | 18.1                       | 1.9         |
|                         | 85°                  | 20               | 54.9                       | 9.1         |

It is obvious from these few simple experiments that piperidine is more reactive than morpholine.

#### ACKNOWLEDGMENTS.

In conclusion, the authors have great pleasure in acknowledging their indebtedness to the Carbide and Carbon Chemical Corporation of America and to their Sydney agents, Messrs. Robert Bryce and Co. Ltd., for their kindness in arranging a gift of morpholine for this work.

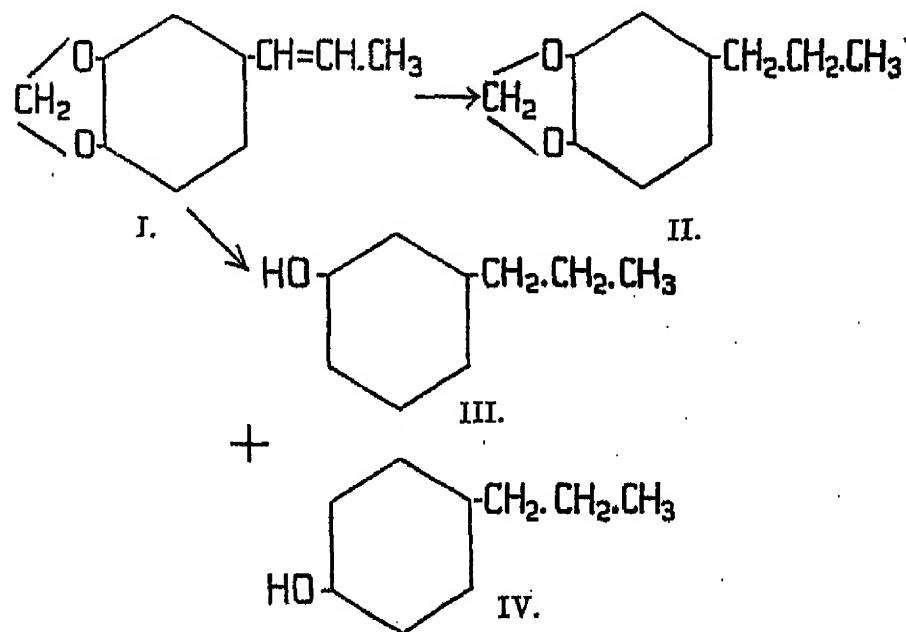
Organic Chemistry Department,  
University of Sydney.

## SOME DERIVATIVES OF 3-N-PROPYL-PHENOL.

By STEWART GORDON COUSIN, B.Sc.,  
and FRANCIS LIONS, B.Sc., Ph.D.

(Manuscript received, November 20, 1936. Read, December 2, 1936.)

The reduction of iso-safrole (I) under certain conditions has been observed to yield appreciable quantities of phenols in addition to the normal product of reduction, dihydrosafrole (II). Thus, reduction with metallic sodium and boiling absolute ethyl alcohol yields mainly dihydrosafrole and 3-n-propylphenol (III), together with some 4-n-propylphenol (IV) (cf. Ciamician and Silber, *Berichte*, 1890, 23, 1162; Ono and Imoto, *J. Chem. Soc. Japan*, 1934, 55, 991-1001).



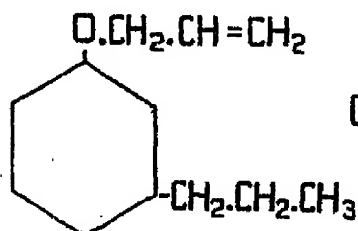
Phenols are also obtained by passage of either I or II together with hydrogen over finely divided nickel at 200° C. (cf. Henrard, *Centralblatt*, 1907, 11, 1512).

Little systematic work on 3-n-propylphenol (III), which is thus readily accessible, has so far been recorded.

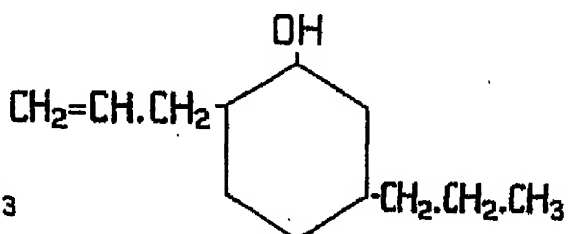
In the present paper complete details for its preparation from isosafrole and the properties of some of its derivatives are discussed. The phenol is best obtained by running hot absolute alcohol on to a vigorously stirred mixture of molten sodium and hot isosafrole under good reflux, and, after solution of the sodium, removal of most of the alcohol by steam distillation, followed by separation of the strongly alkaline aqueous solution of the phenols (III and IV) from the oily layer of II. After recovery from the alkaline solution the dried mixture of phenols is carefully fractionated, the 3-n-propyl phenol being obtained as a practically colourless oily liquid with a not unpleasant characteristic phenolic odour. It boils at  $102^{\circ}/2$  mm. and at  $117^{\circ}/11$  mm. Ciamician and Silber (*loc. cit.*) recorded the boiling point as  $228^{\circ}$ - $230^{\circ}$  at atmospheric pressure.

3-n-Propyl phenol gradually darkens in colour on keeping under ordinary conditions. It is very sparingly soluble in water, and this solution gives a transient blue coloration with ferric chloride solution. The alcoholic solution of the phenol is coloured dark green by ferric chloride solution.

Methylation of III with methyl sulphate and alkali gives the known 3-n-propyl anisole boiling at  $212^{\circ}$ - $213^{\circ}/760$  mm., in almost quantitative yield. With sodium ethoxide and benzyl chloride III gives 3-n-propyl phenyl benzyl ether, a colourless, highly refractive oil boiling at  $184^{\circ}$ - $185^{\circ}/12$  mm. 3-n-Propyl phenyl p-nitrobenzyl ether is a crystalline solid melting at  $43^{\circ}$ . The allyl ether (V) is a colourless highly refractive oil boiling at  $125^{\circ}$ - $126^{\circ}/13$  mm. It is readily isomerised by heating to about  $230^{\circ}$  to a phenol—probably 3-n-propyl-6-allyl phenol (VI)—which boils at  $142^{\circ}$ - $144^{\circ}/16$  mm.



V.



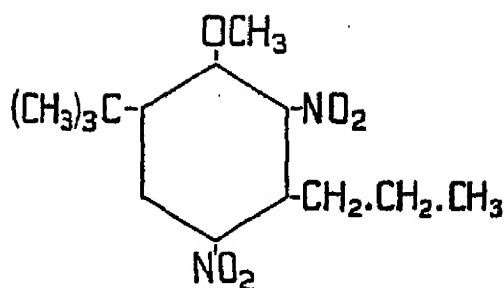
VI.

When boiled with acetic anhydride 3-n-propyl phenol forms 3-n-propylphenyl acetate, a pleasant smelling ester

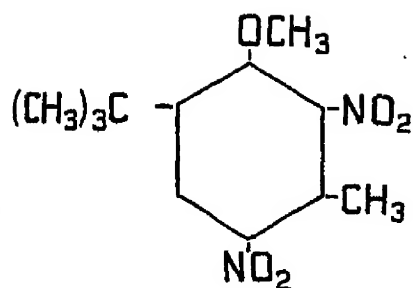
boiling at 238°-240°/762 mm., which gives no colour with alcoholic ferric chloride solution. On the other hand, when heated with acetic anhydride in presence of a little concentrated sulphuric acid, an acetyl group enters the ring and a pale brown oily substance boiling at 121°-123°/18 mm. can be obtained, which gives a violet colour with alcoholic ferric chloride solution, and can be made to give an oxyacetic acid melting at 73° (cf. Koelsch, *Journ. Amer. Chem. Soc.*, 1931, 53, 304-305). 3-n-Propylphenyl benzoate melts at 114°, whilst the 3:5-dinitrobenzoate, which can be obtained by the method of Phillips and Keenan (*Journ. Amer. Chem. Soc.*, 1931, 53, 1924), melts at 77°. Treatment of 3-n-propyl phenol with ethyl chloroformate in presence of aqueous alkali readily yields the ethyl carbonic ester, a pleasant smelling ester boiling at 140°-142°/14 mm. 3-n-Propyl phenoxyacetic acid, melting at 70°, is readily prepared by the method of Koelsch (*loc. cit.*).

Solution of 3-n-propyl phenol in concentrated sulphuric acid followed by treatment with strong nitric acid leads to formation of 2:4:6-trinitro-3-n-propyl phenol, a pale yellow, light-sensitive strongly acidic substance melting at 66°. Bromination of 3-n-propyl phenol in acetic acid solution readily yields 2:4:6-tribromo-3-n-propyl phenol, a colourless solid melting at 85°.

In an effort to find possible outlets for the utilisation of 3-n-propyl phenol, it was decided first to attempt the preparation of 3-n-propyl-6-tertiary butyl 2:4-dinitro anisole VII, a homologue of "Musk Ambrette". The chemistry of the natural musks has only been completely elucidated in recent years, chiefly by Ruzicka and his collaborators (cf. e.g. *Annual Reports of the Chemical Society*, 1926, 23, 112-119). Artificial substances having powerful musk odours have, however, long been known and valued in perfumery. Almost without exception these are aromatic substances with several nitro groups and an isopropyl, tertiary butyl, or similar group attached to the same benzene ring. One of the most valued is "Musk Ambrette", 3-methyl-6-tertiary butyl-2:4-dinitro anisole (VIII), whose correct constitution has been assigned recently by Zeide and Dubinin (*J. Gen. Chem.*, U.S.S.R., 1932, 2, 455-471; cf. *Chemical Abstracts*, 1933, 27, 961). Summaries of the properties, uses and manufacture of these artificial musks are given by A. Wagner (*Chemiker*



VII.



VIII.

*Zeitung*, 1927, 623) and in Ullman's *Encyclopædia der Technischen Chemie*, 1931, 8, 847.

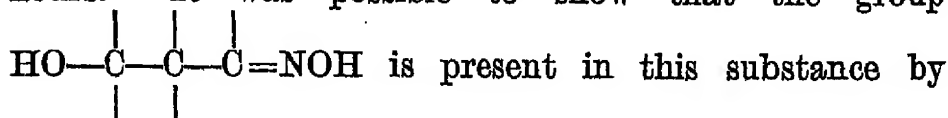
3-n-Propyl anisole, on treatment in the cold with tertiary butyl chloride and anhydrous aluminium chloride, gives a 60 per cent. yield of 3-n-propyl-6-tertiary butyl anisole (IX), an oil boiling at 129°-132°/15 mm., which on nitration with fuming nitric acid in ice-cold acetic anhydride solution yields the dinitro compound VII in 45 per cent. yield. It is a pale yellow, light-sensitive crystalline solid melting at 45°-46°, insoluble in water, but soluble in the usual organic solvents and possessing a very definite sweet musk odour which is well brought out in alcoholic solution.

In a second series of experiments a number of homologues of 3-n-propyl phenol were prepared in order to ascertain whether their germicidal powers were sufficiently marked to render them of outstanding value. The effect of adding alkyl chains to the nuclei of phenolic substances in increasing the phenol coefficients has been frequently observed (cf. e.g. Johnson and Lane, *Journ. Amer. Chem. Soc.*, 1921, 43, 348; Dohme, Cox and Miller, *ibid.*, 1926, 1688; Klarman and co-workers, *ibid.*, 1933, 55, 2576, 4657; Coulthard Marshal and Pyman, *J.C.S.*, 1930, 280).

By utilisation of the Nencki reaction (heating of a phenol with a fatty acid and anhydrous zinc chloride) following the general directions of Brewster and Harris (*Journ. Amer. Chem. Soc.*, 1930, 52, 4866), it has been possible to prepare from 3-n-propyl phenol, 3-n-propyl-6-acetyl phenol (X), 3-n-propyl-6-propionyl phenol (XI), 3-n-propyl-6-n-butyryl phenol (XII) and 3-n-propyl-6-n-valeryl phenol (XIII).

All these phenolic ketones were light yellow viscous liquids with characteristic rather unpleasant clinging odours. Their alcoholic solutions gave purple colorations with ferric chloride, or light-brown when very dilute. When treated with anhydrous stannic chloride in dry ether they gave white fibrous crystalline compounds of

indefinite melting point which decomposed readily on heating or even exposure to air (c.f. Pfeiffer, *Annalen*, 1910, 376, 285-310). Characteristic crystalline derivatives were difficult to prepare (cf. von Anwers, Hilliger and Wulf, *Annalen*, 1921, 429, 190-426). Crystalline semicarbazones of XI and XII were obtained, but the most suitable crystalline derivatives were the oxyacetic acids prepared by the method of Koelsch (*loc. cit.*). After several fruitless attempts the oxime of X was eventually prepared by refluxing the ketone in alcoholic solution with hydroxylamine hydrochloride and barium carbonate for twelve hours. It was possible to show that the group



making use of Ephraim's observation (*Berichte*, 1931, 64, 1210) that substances containing this grouping will precipitate copper from any solution in which copper salts and the oxime are mutually soluble with the exception of hydrochloric acid in which in all cases the copper complex is soluble. 3-n-Propyl-6-acetyl phenol oxime reacted with copper acetate in concentrated or dilute acetic acid, in absolute alcohol or in 50 per cent. alcohol to give a voluminous green precipitate soluble in hydrochloric acid. The phenolic ketone X thus has the structure of an o-hydroxyacetophenone assigned to it, rather than that of a p-hydroxyacetophenone; and the homologous ketones were considered to be analogously constituted. The difficulty of preparation of derivatives involving the hydroxyl or carbonyl groups also supports this formulation.

The ketones X-XIII were readily reduced by Clemmensen's method (*Berichte*, 1913, 46, 1837; 1914, 47, 51) to the corresponding alkyl 3-n-propyl phenols, respectively 3-n-propyl-6-ethyl phenol (XIV), 3:6-di-n-propyl phenol (XV), 3-n-propyl-6-n-butyl phenol (XVI) and 3-n-propyl-6-n-amyl phenol (XVII). When quite pure these are colourless oils insoluble in water but quite soluble in the usual organic solvents. They dissolve in sodium hydroxide solution, but the sodium salts are precipitated by excess sodium hydroxide. They possess rather unpleasant faint but persistent odours, and in alcoholic solution give green colours with ferric chloride. Treated with chloracetic acid and alkali by the method of Koelsch (*loc. cit.*) they all yield the corresponding oxyacetic acids. Preliminary experiments have shown that their

phenol coefficients for *B. typhosus* are considerably higher than unity, but a more complete discussion of these is reserved for the present.

Mercuration of 3-n-propyl phenol with excess of mercuric acetate in alcohol containing acetic acid, according to the method of Henry and Sharp (*J.C.S.*, 1926, 2434) can be effected, but the product is difficult to purify and of indefinite melting point.

Finally, it should be recorded that certain diazonium salts will couple with 3-n-propyl phenol, the resulting azo compounds being brown in colour.

#### EXPERIMENTAL.

*Reduction of Iso-safrole.*—Sufficient hot absolute alcohol was run on to metallic sodium (200 grams), in a three-necked five-litre round-bottomed flask fitted with a good mechanical stirrer, an efficient reflux condenser, and a dropping funnel, to cause the metal to melt. Hot isosafrole (200 grams) was then stirred in, followed by boiling absolute ethyl alcohol (2 litres), run in as rapidly as possible whilst keeping the reaction under control. The final solution of the sodium was aided by heating, and at the completion of the reaction most of the alcohol was distilled off in steam, leaving a strongly alkaline aqueous solution of the phenols and an upper layer of dihydro safrole, which was separated after cooling, with the aid of ether. The alkaline solution was acidified and the liberated phenols were taken up and dried in ether, the solvent removed and the phenols distilled. The main fraction boiling at 227°-230°/760 mm. was collected and redistilled *in vacuo*. The pure 3-n-propyl phenol boils at 124°-125°/18 mm., at 117°-118°/11 mm. and at 102°/2 mm. The yield in different preparations varied between 50 and 65 grams.

A tarry residue was always obtained from the first fractional distillation. It was taken up in alkali, the solution boiled with activated carbon, filtered and acidified, and the liberated oil dried in ether, and finally distilled *in vacuo*. A main fraction boiling at 127°-129°/18 mm. was isolated. It boiled at 230°-231°/758 mm., and gave a methyl ether boiling at 214°-216°/758 mm. when treated with dimethyl sulphate and alkali. Treated with alkali and chloracetic acid, according to the method of Koelsch, it gave an oxyacetic acid melting at 73°. This, on titration, was found to have an equivalent weight of 192. 4-n-Propyl phenol boils at 230°-232°/759 mm., whilst its methyl ether



boils at 215°-216°/760 mm. according to Beilstein, 4th Ed., Vol. VI, p. 500.

The calculated equivalent weight of a propyl phenoxy-acetic acid is 194. Hence, this second substance appears to be 4-n-propyl phenol. Unfortunately, an authentic specimen was not available for comparison.

*3-n-Propyl anisole.* Ciamician and Silber (*loc. cit.*) prepared this ether by methylation of III with methyl iodide. A better method is to use dimethyl sulphate and alkali, which gives practically quantitative yields. The ether is a colourless highly refractive oil with an odour similar to safrole, and boils at 212°-213°/760 mm.

*3-n-Propyl phenyl benzyl ether.* 3-n-Propyl phenol (13.5 grams) and benzyl chloride (13 grams) were added to a solution of sodium (2.3 grams) in ethyl alcohol (30 c.c.) and the resulting mixture was refluxed for six hours. After cooling, dry ether (200 c.c.) was added, the precipitated sodium chloride filtered off, and after removal of the solvent the residual oil fractionated under reduced pressure. A colourless highly refractive oil (15 grams) boiling at 184°-185°/12 mm. was collected.

Found: C=84.8, H=7.9%; calculated for  $C_{16}H_{18}O$ , C=85.0, H=8.0%.

*3-n-Propyl phenyl p-nitrobenzyl ether.* The oily product obtained by heating together for three hours p-nitrobenzyl chloride (5 grams) and a solution of 3-n-propyl phenol (4 grams) and sodium ethoxide (from sodium, 1 gram) in ethyl alcohol (20 c.c.) was taken up in ether, washed with sodium hydroxide solution and dried. After removal of the ether and standing, the oil slowly crystallised. After recrystallisation from alcohol it melted at 43°.

Found: C=70.4, H=6.1%; calculated for  $C_{16}H_{17}O_3N$ , C=70.8, H=6.3%.

*3-n-Propyl phenyl allyl ether V.* Finely powdered anhydrous potassium carbonate (45 grams) was added to a cold solution of 3-n-propyl phenol (32 grams) and allyl iodide (50 grams) in dry acetone (50 c.c.) and the mixture thoroughly shaken. It became warm, and was allowed to stand overnight, after which it was refluxed for eight hours. Water was added, the separated oil taken up, washed and dried in ether, and after removal of the solvent distilled *in vacuo*. The allyl ether came over as a colourless highly refractive oil (35 grams) boiling at 125°-126°/13 mm.

Found: C=81.4, H=9.0%; calculated for  $C_{12}H_{16}O$ , C=81.8, H=9.1%.

This ether has a pleasant faint smell. It does not give a coloration with ferric chloride in alcoholic solution.

*3-n-Propyl-6-allyl phenol VI.* 3-n-Propyl phenyl allyl ether (25 grams) in an all-glass apparatus was carefully heated in a metal bath. When the temperature (thermometer bulb in liquid) had reached 230°, ebullition suddenly occurred and the temperature rose rapidly to 240°. The liquid was finally heated to 260° for ten minutes. After cooling the alkali-soluble portion of the oil (practically all of it) was separated, dried and distilled *in vacuo*. A fraction (21 grams) boiling at 142°-144°/16 mm. was collected.

Found: C=81.5, H=9.2%; calculated for  $C_{12}H_{16}O$ , C=81.8, H=9.1%.

The alcoholic solution of this phenol gave a brown coloration with ferric chloride. Treated with chloracetic acid and alkali by the method of Koelsch (*loc. cit.*) it gave *3-n-propyl-6-allyl oxyacetic acid*, which melts at 47°, and was found on titration to have an equivalent weight of 231.  $C_{14}H_{18}O_3$  requires E.W.=234.

When VI was refluxed with powdered potassium hydroxide in a partial vacuum for three hours, the boiling point was lowered to 137°-138°/16 mm., and the product would no longer form an aryloxy acetic acid. Apparently it had been converted into *3-n-propyl-6-propenyl phenol*. Attempts to reduce this with sodium and absolute alcohol were fruitless.

*3-n-Propyl phenyl acetate.* 3-n-Propyl phenol (10 grams) and acetic anhydride (20 c.c.; excess) were refluxed gently together for three hours. After destruction of the excess acetic anhydride by overnight contact with very weak hydrochloric acid (500 c.c.) the precipitated oil was taken up in ether, washed free from acid with sodium carbonate solution, dried and the solvent removed. The residual oil (9 grams) distilled at 238°-240°/762 mm.

Found: C=73.9, H=7.6%; calculated for  $C_{11}H_{14}O_2$ , C=74.2, H=7.9%.

This ester is colourless, and does not give a coloration with alcoholic ferric chloride solution. It has a definite pleasant smell, and can be readily hydrolysed back to 3-n-propyl phenol with alkali.

Treatment of a solution of 3-n-propyl phenol (10 grams) in acetic anhydride (25 c.c.) with a few drops of concentrated sulphuric acid led to the development of a transient red colour and the evolution of much heat. After gently

refluxing for two hours, the mixture, which had darkened considerably in colour, was poured into very dilute hydrochloric acid and allowed to remain overnight. The oil was then taken up, washed and dried in ether, and after removal of the solvent, fractionated *in vacuo*. A pale yellow oil boiling at 121°-123°/18 mm. was obtained, which had a definite phenolic odour, was soluble in sodium hydroxide solution and gave a violet coloration with ferric chloride in alcoholic solution.

Found: C=73.8, H=7.8%; calculated for  $C_{11}H_{14}O_2$ , C=74.2, H=7.9%.

The substance thus appears to have been formed by the entrance of an acetyl group into the ring and because of its dissimilarity to the 6-acetyl-3-n-propyl phenol described later is probably 4-acetyl-3-n-propyl phenol. In agreement with this formulation it was found possible by suitable treatment with chloracetic acid and alkali to prepare the aryloxyacetic acid—presumably 4-acetyl-3-n-propyl phenoxyacetic acid—as a colourless crystalline solid melting at 73°, with an observed equivalent weight of 229.  $C_{13}H_{16}O_4$  requires an E.W.=236.

*3-n-Propyl phenyl benzoate.* Benzoyl chloride (5 grams) was added over 30 minutes to an ice-cold solution of 3-n-propyl phenol (5 grams) in anhydrous pyridine (30 c.c.). After standing at 0° for one hour, the mixture was poured into water, and the precipitated oil recovered with ether and distilled under reduced pressure. The fraction boiling at 163°-165°/2 mm. solidified on cooling and after recrystallisation from alcohol was obtained in white shining plates melting at 114°.

Found: C=79.8, H=6.9%; calculated for  $C_{16}H_{16}O_2$ , C=80.0, H=6.7%.

*3-n-Propyl-3:5-dinitrobenzoate.* Preliminary attempts to prepare this ester by treatment of either sodium-3-n-propyl phenate in alcoholic solution, or of 3-n-propyl phenol itself in dry ether in presence of anhydrous potassium carbonate with 3:5-dinitrobenzoyl chloride proved abortive. It was eventually obtained by the method of Phillips and Keenan (*loc. cit.*). A solution of 3-n-propyl phenol (1.4 grams) and 3:5-dinitrobenzoyl chloride (2.5 grams) in anhydrous pyridine (20 c.c.) was refluxed gently for one hour. After cooling, the liquid was stirred into 5 per cent. sulphuric acid solution (400 c.c.) and allowed to stand overnight. The precipitate was filtered, washed with water and stirred into 2 per cent. sodium

hydroxide solution, and then finally recrystallised from alcohol. It was obtained thus in pale yellow prisms melting at  $77^{\circ}$ .

Found: C=57.9, H=4.1%; calculated for  $C_{16}H_{14}O_6N_2$ , C=58.2, H=4.2%.

*Ethyl-3-n-propyl phenyl carbonate.* 3-n-Propyl phenol (13.6 grams) was dissolved in a solution of sodium hydroxide (4.2 grams) in water (30 c.c.) and ethyl chloroformate (11 grams) was added gradually with constant shaking. A colourless oil separated. After shaking for one hour the oil was collected and fractionated *in vacuo*. A colourless mobile oil (15 grams) with a distinct, pleasant smell, boiling at  $140^{\circ}$ - $142^{\circ}/14$  mm. was collected.

Found: C=69.0, H=7.5%; calculated for  $C_{12}H_{16}O_3$ , C=69.2, H=7.7%.

*3-n-Propyl phenoxycetic acid* was obtained by the method of Koelsch (*loc. cit.*) as a colourless crystalline substance melting at  $70^{\circ}$ .

Found: C=67.9, H=7.3%; calculated for  $C_{11}H_{14}O_3$ , C=68.0, H=7.2%.

Equivalent weight (by titration) found, 192; calculated for  $C_{11}H_{14}O_3$ , E.W.=194.

*2:4:6-Trinitro-3-n-propyl phenol.* 3-n-Propyl phenol (5 grams) was warmed on the water-bath with concentrated sulphuric acid (15 c.c.) for 15 minutes. The reddish-brown solution was then cooled and poured into concentrated nitric acid (D 1.42; 50 c.c.) and the resulting solution was heated at  $100^{\circ}$  for one hour. Copious red fumes were evolved and the liquid finally became yellow. When poured into ice water a pale yellow oil (7 grams) separated and soon crystallised. Recrystallised from methyl alcohol it was obtained in clusters of pale yellow prisms melting at  $65^{\circ}$ - $66^{\circ}$ .

Found: C=39.4, H=3.1%; calculated for  $C_9H_9O_7N_3$ , C=39.9, H=3.3%.

This homologue of picric acid is definitely acidic, and dissolves readily in alkaline carbonate solutions. Exposure of the solid substance to sunlight causes the yellow colour to change rapidly to brown, the crystals being very sensitive to light.

*2:4:6-Tribromo-3-n-propyl phenol.* A solution of bromine (9.6 grams) in glacial acetic acid (10 c.c.) was gradually added to a solution of 3-n-propyl phenol (2.5 grams) in glacial acetic acid (10 c.c.), the temperature being maintained below  $20^{\circ}$ . Hydrogen bromide was

evolved, and finally the tribromophenol was obtained solid by pouring the acetic acid solution into water. Recrystallised from methyl alcohol, it was obtained in colourless needles melting at  $85^{\circ}$ .

Found: C=28.8, H=2.0%; calculated for  $C_9H_9OBr_3$ , C=29.0, H=2.4%.

*3-n-Propyl-6-tertiary-butyl anisole IX.* 3-n-Propyl anisole (15 grams) was carefully added to pure powdered anhydrous aluminium chloride (3.2 grams) in a flask which was then cooled in a freezing mixture and evacuated. Tertiary butyl chloride (9.2 grams) was then allowed to drop in slowly, and the reaction mixture was kept cold *in vacuo* until it crystallised (about two hours). The vacuum was then released and the aluminium salts treated carefully with ice. The liberated oil was washed and dried in ether and finally fractionated *in vacuo*, the fraction boiling at  $129^{\circ}$ - $132^{\circ}$ /15 mm. (12.5 grams; 60% of theory) being collected.

Found: C=81.1, H=10.0%; calculated for  $C_{14}H_{22}O$ , C=81.6, H=10.7%.

This ether is a colourless oil with a characteristic odour quite distinct from that of 3-n-propyl anisole.

*3-n-Propyl-6-tertiary-butyl-2:4-dinitro anisole VII.* After some preliminary trials the nitration of IX was effected as follows: Acetic anhydride (40 grams) (in a three-necked flask fitted with a good stirrer and two dropping funnels) was cooled to  $-5^{\circ}$  and kept vigorously stirred whilst a solution of IX (7 grams) in acetic anhydride (15 c.c.) was added drop by drop from one funnel, and freshly redistilled fuming nitric acid (D 1.5; 40 grams) added gradually from the other, the temperature being maintained below  $0^{\circ}$  throughout the addition and for 30 minutes afterwards. The temperature was then allowed to rise to  $25^{\circ}$ , and after a further 30 minutes the reaction mixture was poured on to ice. The semi-solid oil which separated was collected and submitted to a short steam distillation to remove volatile impurities. It was then taken up, washed and dried in ether and the solvent removed. The residual oil crystallised, and after recrystallisation from absolute ethyl alcohol pale yellow needles melting at  $41^{\circ}$  were obtained (yield 45%).

Found: C=49.1, H=5.4, N=12.5%; calculated for  $C_{14}H_{19}O_7N_3$ , C=49.3, H=5.6, N=12.3%.

This substance is insoluble in water, but soluble in most organic solvents, and possesses a definite sweet musk

odour, which is well brought out in solution in ethyl alcohol. Alcoholic solutions show a marked tendency to acquire a brown colour, particularly when exposed to light and air. The solid is also very sensitive to sunlight.

*Preparation of the phenolic ketones X-XIII.* A general Nencki reaction was used in each instance, the preparation of 3-n-propyl-6-acetyl phenol X being typical. 3-n-Propyl phenol (40 grams) and glacial acetic acid (50 grams), containing anhydrous zinc chloride (40 grams) in solution were refluxed at  $180^{\circ}$  for five hours. After standing overnight, the thick liquid was treated with ice and dilute hydrochloric acid, and the oil extracted, washed with sodium carbonate, dried and fractionated *in vacuo*. The fraction boiling at  $124^{\circ}$ - $136^{\circ}$ /14 mm. was collected and redistilled, 20 grams of a yellow oil boiling at  $128^{\circ}$ - $131^{\circ}$ /16 mm. being obtained (40% of theory). On redistillation at 0.7 mm. it boiled at  $93^{\circ}$ .

Found: C=73.8, H=7.9%; calculated for  $C_{11}H_{14}O_2$ , C=74.1, H=7.9%.

In common with the other ketones of this series, this ketone X gave a deep purple coloration when its alcoholic solution was treated with ferric chloride solution.

The derived aryloxyacetic acid, 3-n-propyl-6-acetyl phenoxyacetic acid, melted at  $52^{\circ}$  and on titration with standard alkali was found to have an equivalent weight of 231.5, the theoretical value being 236.

*3-n-Propyl-6-propionyl phenol XI.* Yield 38% of theory. Boiling range,  $124^{\circ}$ - $125^{\circ}$ /13 mm. or  $90^{\circ}$ /0.7 mm.

Found: C=74.2, H=8.5%; calculated for  $C_{12}H_{16}O_2$ , C=75.0, H=8.7%.

The derived 3-n-propyl-6-propionyl phenoxyacetic acid melts at  $62^{\circ}$ .

Found equivalent weight=242; calculated for  $C_{14}H_{18}O_4$ , E.W.=250.

The semicarbazone of XI, difficult to prepare, melts at  $132^{\circ}$ .

*3-n-Propyl-6-n-butyryl phenol XII.* Yield 40% of theory. Boiling range,  $130^{\circ}$ - $132^{\circ}$ /19 mm., or  $87^{\circ}$ - $88^{\circ}$ /0.7 mm.

Found: C=76.0, H=8.5%; calculated for  $C_{13}H_{18}O_2$ , C=75.7, H=8.7%.

The derived 3-n-propyl-6-n-butyryl phenoxyacetic acid melts at  $67^{\circ}$ .

Found: Equivalent weight=259; calculated for  $C_{15}H_{20}O_4$ , E.W.=264.

The semicarbazone of XII was a yellow solid, melting at 175°.

In the preparation of XII a small amount of a fraction boiling at 151°-153°/19 mm. was obtained. It gave a purple colour with ferric chloride in alcoholic solution.

*3-n-Propyl-6-n-valeryl phenol XIII.* Yield 30% of theory. Boiling range, 127°-129°/18 mm., or 84°-85°/0.7 mm.

Found: C=76.6, H=8.9; calculated for  $C_{14}H_{20}O_2$ , C=76.4, H=9.1%.

The derived *3-n-propyl-6-n-valeryl phenoxyacetic acid* melts at 69°.

Found: Equivalent weight=274; calculated for  $C_{16}H_{22}O_4$ , E.W.=278.

A small amount of a substance boiling at 139°-141°/19 mm. was obtained from the preparation of XIII.

Attempts to prepare esters of the phenolic ketones X-XIII using the Schotten-Baumann reaction all failed. Treatment of them with anhydrous ethereal stannic chloride led to the separation of white fibrous crystalline compounds of indefinite melting point. The *oxime* of *3-n-propyl-6-acetyl phenol* was eventually prepared by refluxing a well-stirred mixture of X with hydroxylamine hydrochloride and barium carbonate in methylated spirit for twelve hours. The yield even then was poor, the product consisting of white needles (from petroleum ether) melting at 74°.

Found: N=7.0%; calculated for  $C_{11}H_{15}O_2N$ , N=7.3%.

This oxime dissolved easily in glacial acetic acid or ethyl alcohol, and from these solutions of copper acetate in the same solvents at once precipitated a very voluminous green precipitate soluble in hydrochloric acid. Similar behaviour was observed with solutions in 50 per cent. acetic acid or 50 per cent. alcohol. Nickel salts in alcohol were partially precipitated with an alcoholic solution of the oxime, whilst ferric chloride gave no precipitate but an intense brown-black coloration even at very great dilution.

*Reduction of the phenolic ketones X-XIII.* The method employed for reduction of the ketones was essentially that of Clemmensen (*loc. cit.*). The yields of pure dialkyl phenols obtained varied from 50 to 65 per cent. They were all colourless or pale yellow oils insoluble in water, but readily soluble in organic solvents. They dissolved in sodium hydroxide solution, but are reprecipitated as

sodium salts on addition of excess NaOH. They have unpleasant clinging odours and in alcohol give green colours with ferric chloride. Preliminary trials without emulsification showed that they possessed values higher than phenol against *B. typhosus*.

*3-n-Propyl-6-ethyl phenol XIV*. Boil at 126°-127°/15 mm. or at 84°-85°/0.7 mm.

Found: C=79.8, H=9.9%; calculated for  $C_{11}H_{16}O$ , C=80.4, H=9.8%.

The derived *3-n-propyl-6-ethyl phenoxyacetic acid* melts at 75°.

Found: E.W.=220; calculated for  $C_{13}H_{18}O_3$ , E.W.=222.

Treated with dimethyl sulphate and alkali XIV is readily converted into its methyl ether *3-n-propyl-6-ethyl-anisole*, a colourless liquid boiling at 112°-114°/26 mm. and possessing a strong odour of aniseed. On oxidation with alkaline permanganate this ether gave a definite yield of m-methoxy benzoic acid (melting point 108°; E.W. found, 148; calculated, 152), together with a small amount of another acid melting above 250° and being possibly methoxy terephthalic acid (M.P. 280°).

*3:6-Di-n-propyl phenol XV*. Boils at 131°-132°/15 mm. or at 88°-89°/0.7 mm.

Found: C=79.9, H=10.2%; calculated for  $C_{12}H_{18}O$ , C=80.9, H=10.1%.

The derived *3:6-di-n-propyl phenoxyacetic acid* melts at 69°.

Found: E.W.=234; calculated for  $C_{14}H_{20}O_3$ , E.W.=236.

*3-n-Propyl-6-n-butyl phenol XVI*. Boils at 137°-139°/30 mm. or at 87°/0.8 mm.

Found: C=81.3, H=10.6%; calculated for  $C_{13}H_{20}O$ , C=81.2, H=10.4%.

The derived *3-n-propyl-6-n-butyl phenoxyacetic acid* melts at 67°.

Found: E.W.=245; calculated for  $C_{15}H_{22}O_3$ , E.W.=250.

*3-n-Propyl-6-n-amyl phenol XVII*. Boils at 127°-128°/14 mm. or at 81°/0.7 mm.

Found: C=81.9, H=10.8%; calculated for  $C_{14}H_{22}O$ , C=81.6, H=10.7%.

The derived *3-n-propyl-6-n-amyl phenoxyacetic acid* melts at 64°.



Found : E.W.=261 ; calculated for  $C_{16}H_{24}O_3$ , E.W.=264.

*Attempts to mercurate 3-n-propyl phenol.* Treatment of III with excess mercuric acetate in alcohol containing about 40% of glacial acetic acid (cf. Henry and Sharp, *loc. cit.*) under reflux for one hour, followed by overnight standing at  $0^\circ$ , led to the formation of a sticky red mass (after precipitation with water). On boiling with alcohol, it lost its stickiness but did not become crystalline. It was dissolved in sodium hydroxide solution, and after treatment with charcoal acetic acid was added to this solution. The white substance so obtained melted at  $220^\circ$ - $225^\circ$ .

Attempts to prepare a monomercurated compound from III led to formation only of indefinite products.

*Coupling of 3-n-propyl-phenol with diazo salts.*

1. Diazotised p-toluidine coupled readily with III in alkaline solution to give a brown crystalline dye, obtained in needles melting at  $125^\circ$ - $127^\circ$  after recrystallisation from alcohol.

2. Diazotised m-nitraniline coupled with III to give a difficultly crystallisable substance obtained from alcohol in light brown needles melting at  $139^\circ$ - $142^\circ$ .

3. The products obtained by coupling III with diazotised aniline, 2:4-dichloroaniline and  $\beta$ -naphthylamine, were brown oils.

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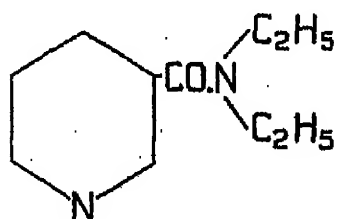
## NICOTINYL MORPHOLINE.

By RITA H. HARRADENCE  
and FRANCIS LIONS, B.Sc., Ph.D.

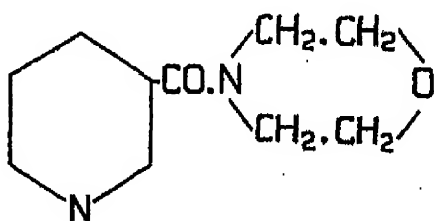
(Manuscript received, November 20, 1936. Read, December 2, 1936.)

In a recent paper Warburg, Christian and Griesse (*Biochemisches Zeitschrift*, 1935, 279, 143-144) have shown that the co-enzyme prepared from red blood cells contains carbohydrate, phosphoric acid, adenine and a pyridine substance which on hydrolysis yields nicotinic acid amide (I). The activity of the preparation is proportional to the content of I, and the most active preparations contained about 25 per cent. of I, which is the active group. The pyridine portion of the co-enzyme is intimately concerned in the oxidation of hexose monophosphate to phosphohexonic acid, taking up two hydrogen atoms in the process and then being again reoxidised by the alloxazine of the yellow enzyme. Nicotinic acid amide obtained by hydrolysis from the co-enzyme is itself catalytically inactive, but the biological significance of the pyridine moiety in the co-enzyme cannot be over emphasised.

The display of powerful physiological action by certain substituted derivatives of nicotinamide is, consequently, readily understandable, and attention should be drawn to "Coramine"—a preparation containing the diethylamide of nicotinic acid (II)—which is considered one of the best respiratory analeptics at the present time. It was therefore considered worth while by the authors to prepare the acid amide from nicotinic acid and morpholine—nicotinyl morpholine (III)—in order that its physiological action

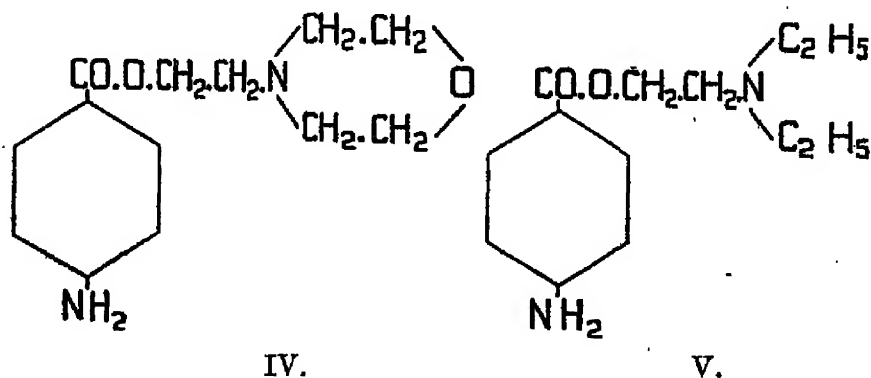


II.



III.

might be investigated, III differing from II only in having a morpholine residue substituted for a diethylamine residue. That such a substitution might be expected to lead to very marked alteration in the physiological action is to be expected, but, at the same time, it should be recalled that Gardner and Haenni (*Journ. Amer. Chem. Soc.*, 1931, 53, 2763) have shown that  $\beta$ -4-morpholino ethyl p-aminobenzoate (IV) [the morpholine analogue of procaine (V)] has similar powerful local anæsthetic activity and low toxicity.



Nicotinyl morpholine was obtained by prolonged refluxing of ethyl nicotinate with excess of morpholine. It is a colourless viscous liquid, and gives well crystallised derivatives such as the picrate, aurichloride and methiodide. A report on its pharmacological action will be published later.

#### EXPERIMENTAL.

*Nicotinyl morpholine* III was prepared in relatively small yield only by prolonged refluxing (80 hours) of ethyl nicotinate (40 grams) with morpholine (50 grams; excess), followed by careful fractionation of the brown reaction liquid in a vacuum. A colourless oil boiling at  $210^{\circ}$ - $215^{\circ}/22$  mm. was collected. It solidified on cooling and was found to be a mixture of much nicotinic acid and some nicotinyl morpholine. Eventually, the base III was separated by solution in ether, in which it is sparingly soluble, whilst nicotinic acid is practically insoluble. After removal of the ether, the base was again distilled in a vacuum, and was obtained as a colourless viscous liquid boiling at  $192^{\circ}/6$  mm.

Found : C=62.3, H=6.6%; calculated for  $C_{10}H_{12}O_2N_2$ , C=62.5, H=6.3%.

The relatively large amount of hydrolysis of the ester, ethyl nicotinate, presumably by traces of water in the presence of the secondary base, morpholine, is worthy of notice. No special precautions to exclude moisture rigidly were observed; and in later experiments the action of *anhydrous* morpholine on *anhydrous* ethyl nicotinate will be investigated.

The *Picrate* of nicotinyl morpholine can readily be prepared from the base and picric acid in alcoholic solution. It crystallises from alcohol, in which it is but sparingly soluble in the cold, in bright yellow needles melting at 174°-175°.

Found: N=16.4%. Calculated for  $C_{16}H_{15}O_9N_5$ , N=16.6%.

The *Methiodide* is readily formed by heating together the base III and excess methyl iodide at 100°. Twice recrystallised from alcohol, it was obtained in cream coloured needles melting at 211°-212°.

Found: C=39.4, H=4.9%; calculated for  $C_{11}H_{16}O_2N_2I$ , C=39.5, H=4.5%.

The *Aurichloride* was obtained in bright yellow needles melting at 168° by adding auric chloride to a hot solution of nicotinyl morpholine in dilute hydrochloric acid and then allowing the solution to cool.

Found: Au=37.0%; calculated for  $C_{10}H_{12}O_2N_2, HAuCl_4$ , Au=37.0%.

#### ACKNOWLEDGMENT.

In conclusion, the authors have great pleasure in acknowledging their indebtedness to the Carbide and Carbon Chemical Corporation of America, and to their Sydney agents, Messrs. Robert Bryce and Co. Ltd. for their kindness in arranging a gift of morpholine for this work.

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University of Sydney.

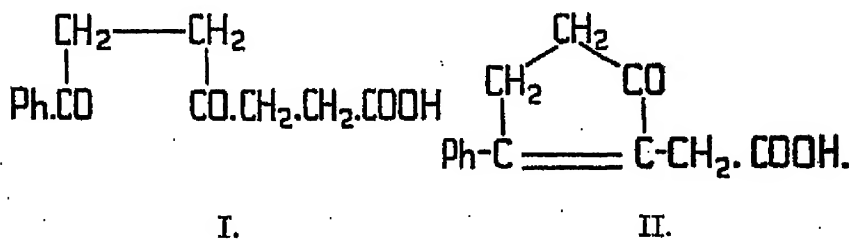
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# N-PHENYL PYRROLES DERIVED FROM PHENACYL LÆVULINIC ACID.

By MURIEL GERTRUDE HOLDSWORTH, M.Sc.,  
and FRANCIS LIONS, B.Sc., Ph.D.

(Manuscript received, November 25, 1936. Read, December 2, 1936.)

Hydrolysis of fural acetophenone, first with methyl alcoholic hydrochloric acid and then with hot aqueous hydrochloric acid, leads to the formation of phenacyl lævulinic acid (I) (cf. Kehler and Igler, *Berichte*, 1899, 32, 1178; Kehler, *ibid.*, 1901, 34, 1263). Solution of this pale yellow acid in hot dilute sodium hydroxide solution causes rapid internal condensation, and on cooling and acidifying, the solution deposits colourless crystals of an acid  $C_{13}H_{12}O_3$ , melting at  $138^\circ$ , which is almost certainly 3-phenyl- $\Delta^2$ -cyclopenten-1-onyl-2-acetic acid (II). Examination of (II) shows that it readily yields a semi-

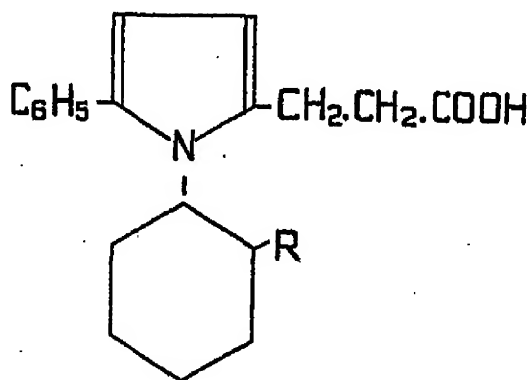


carbazone and a phenylhydrazone; and that on reduction with sodium amalgam it behaves as a typical  $\alpha\beta$  unsaturated ketone, being reduced at the olefine double bond to 3-phenyl cyclopentan-1-onyl-2-acetic acid (III), which melts at  $132^\circ$ , and also forms a semicarbazone and a phenylhydrazone.

Kehler (*loc. cit.*) has shown that phenacyl lævulinic acid (I) reacts with ammonia to form 2-phenyl pyrrole-5- $\beta$ -propionic acid. Since 1:4-diketones usually react just as easily with primary amines to form N-substituted pyrroles it was decided to condense I with a series of ortho substituted anilines, primarily with the object of obtaining substances capable of resolution into enantiomorphous

forms, their asymmetry being due to restricted rotation about the bond joining the pyrrole and the N-phenyl nuclei. The acid I is a favourable starting material in such syntheses as it supplies two of the blocking groups usually necessary (one blocking group can be sufficient in the diphenyl series) (cf. Leslie and Turner, *J.C.S.*, 1933, 1588). Further, one of these groups contains a very useful salt-forming carboxyl group, whilst the other, the phenyl group, is of peculiar interest in studies of this type because the value of the "obstacle" effect it can contribute has not yet been fully studied. Considered as a flat hexagon, a suitably orientated ortho substituent phenyl group of a binuclear system might conceivably allow the second nucleus with small ortho substituents to rotate freely, whereas, if the benzene ring must be looked upon as not flat, but as possessing a definite "bulge" (cf. e.g. J. M. Robertson, *Proc. Roy. Soc.*, 1933, 140A, 79) the obstacle effect would be greater and stereoisomerism due to restricted rotation would occur.

In this paper a study of the condensation of aniline with phenacyl lævulinic acid under different conditions is described, the product in each instance being 1 : 2-diphenyl pyrrole-5- $\beta$ -propionic acid (IV ; R=H).



IV.

The preparation of a series of ortho substituted N-phenyl-2-phenyl-pyrrole-5- $\beta$ -propionic acids [IV ; R = -Cl, -Br, -OCH<sub>3</sub>, -C<sub>2</sub>H<sub>5</sub>, -CH<sub>3</sub>, -C<sub>6</sub>H<sub>5</sub>, -COOH], and of N- $\alpha$ -naphthyl-2-phenyl pyrrole-5- $\beta$ -propionic acid, and N-8'-quinolyl-2-phenyl pyrrole-5- $\beta$ -propionic acid has also been carried out, and these substances are described in the experimental section. They are mostly relatively weak acids, and form alkaloidal salts with reluctance, but some preliminary experiments with the brucine salt of

N-o-carboxyphenyl-2-phenyl pyrrole-5- $\beta$ -propionic acid (IV; R=—COOH) show quite clearly that this substance is resolvable; and an account of its complete resolution will shortly be communicated to the Society.

#### EXPERIMENTAL.

*3-Phenyl- $\Delta^2$ -cyclopenten-1-onyl-2-acetic acid (II).* Phenacyl lœvulinic acid (Kehrer, *loc. cit.*) was dissolved in an excess of 5% sodium hydroxide solution and the resulting liquid boiled for five minutes, filtered, cooled and acidified with hydrochloric acid. A white crystalline precipitate separated and after collection and recrystallisation from ethyl acetate it melted at 138°.

Found: C=72.0, H=5.7%; calculated for  $C_{13}H_{12}O_3$ , C=72.2, H=5.6%.

Treatment of this acid (1 mol.) in alcoholic solution with phenyl hydrazine (1 mol.) led to formation of the yellow crystalline *phenylhydrazone*, which melts at 180°-181°.

Found: C=74.2, H=6.1%; calculated for  $C_{19}H_{18}O_2N_2$ , C=74.5, H=5.9%.

Similarly, addition of semicarbazide hydrochloride (1 gram) and sodium acetate (1 gram), dissolved in a minimum quantity of water to an alcoholic solution of the acid (II), led after a short time to separation of cream-coloured crystals, of the *semicarbazone*. They were collected, and after recrystallisation from hot dilute acetic acid melted at 224°-225°.

Found: C=61.3, H=5.7%; calculated for  $C_{14}H_{15}O_3N_3$ , C=61.5, H=5.5%.

*3-Phenyl-cyclopentan-1-onyl-2-acetic acid (III).* To a solution of the acid II (23 grams) and sodium carbonate (25 grams) in water (75 c.c.) was gradually added sodium amalgam (350 grams of 2.5%) with continual shaking. After standing overnight the mercury was separated, and the alkaline solution acidified. An oil was separated. After washing with water it crystallised and was recrystallised first from carbon tetrachloride and then twice from a mixture of dry acetone and petroleum ether, being thus obtained in colourless needles melting at 132°.

Found: C=71.7, H=6.3%; calculated for  $C_{13}H_{14}O_3$ , C=71.6, H=6.4%.

Treatment of this acid III in alcohol with phenyl hydrazine (1 mol.) led to formation of the *phenylhydrazone*, which separated in colourless prisms melting at 165°.

Found : C=73.8, H=6.8% ; calculated for  $C_{19}H_{20}O_2N_2$ , C=74.0, H=6.5%.

The *semicarbazone*, obtained by treatment of an alcoholic solution of the acid with aqueous semicarbazide acetate melted at 198°-199° after recrystallisation from alcohol.

Found : C=61.2, H=6.5 ; calculated for  $C_{14}H_{17}O_3N_3$ , C=61.1, H=6.2%.

*1:2-Diphenyl pyrrole-5-β-propionic acid* (IV ; R=—H). Several different experiments on the condensation of aniline and phenacyl lævulinic acid under slightly different conditions were carried out, but the product in each instance was the same. Thus, heating together phenacyl lævulinic acid I (1 mol.) and aniline (1 mol.) at 100°, or I (1 mol.) and aniline in excess at 100° ; or heating the components together in boiling alcohol lead always to formation of an acid crystallising from ethyl acetate in pale yellow needles melting at 175°. In a typical experiment phenacyl lævulinic acid (3 grams ; 1 mol.) and aniline (1.2 grams ; 1 mol.) were heated together in a long-necked flask on a rapidly boiling water-bath for three hours. Water commenced to separate almost immediately and the contents of the flask solidified in a very short time. The product was dissolved in dilute sodium hydroxide solution, traces of aniline removed with ether, the solution then boiled with decolourising charcoal, filtered, cooled and acidified. A heavy cream precipitate (4 grams ; yield practically quantitative) was deposited, and was recrystallised first from alcohol, then from ethyl acetate.

Found : C=78.3, H=5.9% ; calculated for  $C_{19}H_{17}O_2N$ , C=78.4, H=5.8%.

This pyrrole derivative is insoluble in water but soluble in alkalis and in ammonia. It is fairly soluble in ether, acetone, ethyl acetate, chloroform and hot alcohol, but less soluble in cold alcohol. The alcoholic solution gives a marked red colour with p-dimethylamino benzaldehyde in presence of dilute hydrochloric acid (Ehrlich's reaction).

*Ethyl-1:2-diphenyl pyrrole-5-β-propionate*. A solution of the acid IV (R=—H) (10.5 grams) in ethyl alcohol (50 c.c.) containing dry hydrogen chloride (1.5 grams) was refluxed for four hours. After removal of the alcohol a solid ester was obtained. Recrystallised from alcohol it formed colourless prisms melting at 102°-103°, soluble in all the usual organic solvents.



Found : C=78.8, H=6.8% ; calculated for  $C_{21}H_{21}O_2N$ , C=79.0, H=6.6%.

Refluxing of this ester (10 grams) with hydrazine hydrate solution (20 grams of 50%) in alcohol (30 c.c.) for four hours leads to formation of the *acid hydrazide of 1:2-diphenyl pyrrole-5- $\beta$ -propionic acid*. After removal of the alcohol the residue was washed with water and then left in contact with a little acetone, when it crystallised. It was recrystallised from a mixture of dry acetone and petroleum ether and obtained in small cream-coloured plates melting at 142°.

Found : C=74.9, H=6.5% ; calculated for  $C_{19}H_{19}ON_3$ , C=74.8, H=6.2%.

This acid hydrazide is soluble in most of the ordinary solvents except petroleum ether. Its decomposition via the azide has not yet been studied.

*Preparation of substituted N-phenyl-2-phenyl pyrrole-5- $\beta$ -propionic acids (IV)*. The methods employed were those evolved in the study of the reaction of aniline with phenacyl lævulinic acid. When the substituted aniline used was a liquid, or of low melting point, the method of heating together the amine (1 mol.) and the acid I (1 mol.) at 100° for two or three hours usually led to good yields of the desired product. Where the base was of higher melting point it was usually more convenient to heat the equimolecular mixture under reflux in alcoholic solution. The yields varied from 30% to 90%. The products were all well crystallised and could be readily purified from a suitable solvent, usually acetone, alcohol or ethyl acetate. Alcoholic solutions of the acids all showed Ehrlich's reaction. Some of the acids were remarkable in that they dissolved easily in potassium hydroxide solution, and in ammonia, but would not dissolve in sodium hydroxide solution.

*1-o-Chlorophenyl-2-phenyl pyrrole-5- $\beta$ -propionic acid (IV ; R=Cl)*. White needles melting at 170°.

Found : C=70.1, H=5.1% ; calculated for  $C_{19}H_{16}O_2NCl$ , C=70.0, H=4.9%.

*1-o-Bromophenyl-2-phenyl pyrrole-5- $\beta$ -propionic acid (IV ; R=Br)*. White prisms melting at 191°.

Found : C=61.5, H=4.4% ; calculated for  $C_{19}H_{16}O_2NBr$ , C=61.1, H=4.3%.

*1-o-Methoxy phenyl-2-phenyl pyrrole-5- $\beta$ -propionic acid (IV ; R=OCH<sub>3</sub>)*. Light yellow needles melting at 162°.

Found : C=74.6, H=6.2% ; calculated for  $C_{20}H_{19}O_3N$ ,  
C=74.8, H=5.9%.

*1-o-Ethoxyphenyl-2-phenyl pyrrole-5-β-propionic acid* (IV ;  
R=OC<sub>2</sub>H<sub>5</sub>). Pale yellow needles melting at 149°.

Found : C=74.9, H=6.4% ; calculated for  $C_{21}H_{21}O_3N$ ,  
C=75.2, H=6.3%.

*1-o-Xenyl-2-phenyl pyrrole-5-β-propionic acid* (IV ; R=  
C<sub>8</sub>H<sub>5</sub>). Colourless prisms melting at 73°.

Found : C=81.6, H=6.0% ; calculated for  $C_{25}H_{21}O_2N$ ,  
C=81.7, H=5.7%.

*1-o-Carboxyphenyl-2-phenyl pyrrole-5-β-propionic acid* (IV ;  
R=—COOH). Colourless prisms melting at 191°.

Found : C=71.4, H=5.2% ; calculated for  $C_{20}H_{17}O_4N$ ,  
C=71.6, H=5.1%.

*1-α-Naphthyl-2-phenyl pyrrole-5-β-propionic acid*. Colour-  
less prisms melting at 130°.

Found : C=80.6, H=5.5% ; calculated for  $C_{23}H_{19}O_2N$ ,  
C=80.9, H=5.5%.

*1-8'-Quinolyl-2-phenyl pyrrole-5-β-propionic acid*. Pale  
yellow needles melting at 182°.

Found : C=77.1, H=5.7% ; calculated for  $C_{22}H_{18}O_2N_2$ ,  
C=77.2, H=5.3%.

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## SOME DERIVATIVES OF DIPHENYL METHYL ARSINE.

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and A. LENCH, B.Sc.

(Manuscript received, November 25, 1936. Read, December 2, 1936.)

The oxide, hydroxynitrate and dichloride of diphenyl methyl arsine have previously been described (THIS JOURNAL, 1934, 68, 77, and 1936, 70, 296). Diphenyl methyl arsine dichloride was found to be slightly soluble in cold benzene and appreciably soluble in the hot solvent; it was also soluble in acetone and extremely soluble in water. These facts suggest that in aqueous solution the compound is hydrolysed to the hydroxychloride and hydrochloric acid, which is consistent with its acid reaction to litmus. The fact that the molecular weight as determined by the cryoscopic method in benzene agrees with that calculated from the formula would indicate that in this solvent the compound is stable, without any tendency to break down into simpler molecules.

The present communication contains a description of the preparation and properties of other derivatives of this arsine.

## EXPERIMENTAL.

*Diphenyl methyl arsine dibromide*,  $Ph_2MeAsBr_2$ , was prepared by adding a solution of bromine in carbon tetrachloride to a solution of diphenyl methyl arsine in the same solvent, with constant stirring. The action, which was strongly exothermic, resulted in the immediate separation of an orange-yellow solid, which was recrystallised from chloroform. If recrystallised slowly it was obtained in the form of colourless rhombohedra, otherwise it separated in small stout prisms, melting with slight decomposition at  $116^\circ C$ . The crystals were highly refractive, strongly lachrymatory, and were found to sublime. The compound was insoluble in carbon tetrachloride, benzene or cold acetone, soluble in hot acetone, giving a solution acid to

litmus, and slowly soluble in cold water. The aqueous solution is also acid to litmus, the compound no doubt being hydrolysed with liberation of hydrobromic acid. The compound was found to decompose slowly on keeping.

Found: Br=39.6, As=18.0 per cent.  $C_{13}H_{13}AsBr_2$  requires Br=39.6, As=18.6 per cent.

*Diphenyl methyl arsine tetrabromide*,  $Ph_2MeAsBr_4$ , was obtained by adding excess of bromine in carbon tetrachloride to a solution of the arsine in the same solvent. A dark red oil separated, and this solidified on standing for a few days. The solid was broken up and washed with carbon tetrachloride, in which it is insoluble. The tetrabromide could not be recrystallised. On dissolving in chloroform and concentrating, the dibromide crystallised from the solution. The compound was found to melt at  $63^{\circ}$ - $64^{\circ}$  C. and slowly gave off bromine when exposed to the air. This accounts for the low bromine result obtained in the analysis.

Found: Br=55.8 per cent.  $C_{13}H_{13}AsBr_4$  requires Br=56.7 per cent.

*Diphenyl methyl arsine diiodide*,  $Ph_2MeAsI_2$ , was obtained by adding a chloroform solution of iodine to one of the arsine. After concentrating the solution it was allowed to stand, when pale yellow prisms separated, together with a small amount of a dark red oil. The latter is probably the tetraiodide, but as it could not be obtained as a solid at the ordinary temperatures it was not analysed. The diiodide was recrystallised from chloroform. Attempts to prepare the diiodide in carbon tetrachloride solution were unsuccessful, the dark oily tetraiodide being obtained. The diiodide crystallised in fine pale yellow prisms which slowly darkened to a red colour on keeping for some weeks. The compound melted at  $104^{\circ}$  C. with decomposition. It was insoluble in benzene and carbon tetrachloride, very soluble in acetone and chloroform and hydrolysed by water. When heated in carbon tetrachloride it changed to the deep red oil.

Found: I=51.6 per cent.  $C_{13}H_{13}AsI_2$  requires I=51.0 per cent.

*Diphenyl methyl hydroxy arsonium chloride*,  $Ph_2MeAs(OH)Cl$ , was prepared by treating diphenyl methyl arsine oxide with 5N hydrochloric acid in hot alcoholic solution. The compound separated on cooling in colourless prisms, which on recrystallisation from hot water melted at  $147^{\circ}$  C. It was found to be fairly soluble in alcohol

and soluble in water giving a solution which was acid to litmus. Like other hydroxy salts, it could be titrated with barium hydroxide solution.

Found: Cl=11.8, As=24.8 per cent. E.Wt.=294.1.  
 $C_{13}H_{13}As(OH)Cl$  requires Cl=12.0, As=25.3 per cent.  
M.Wt.=296.5.

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## CYANOGENETIC GLUCOSIDES IN AUSTRALIAN PLANTS.

PART 6.—AN UNSTABLE CYANOGENETIC CONSTITUENT IN *GOODIA LOTIFOLIA*.

By HORACE FINNEMORE, B.Sc. (Lond.), F.I.C.,  
and DOROTHY K. LARGE, B.Sc.

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(Manuscript received, November 25, 1936. Read, December 2, 1936.)

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*Goodia lotifolia* Salisb., belonging to the family Leguminosæ, occurs as a tall shrub or small tree, bearing yellow flowers, the standard petals of which have a purple base; its short legumes contain from one to three black seeds. On account of the resemblance of its delicate trifoliate leaves to those of clover it is sometimes known as the clover tree. It is found in all the States, especially in the coastal areas, where it favours moist shady situations.

In a communication<sup>(1)</sup> to this Society in 1928, one of us, with Mr. C. B. Cox, B.Sc., gave a short account of the quantitative examination of the leaves of a single bush which was found as an isolated specimen near Middle Harbour. This was strongly cyanogenetic, yielding 0.57 per cent. of hydrocyanic acid calculated on the material dried at 100°. At that time this high percentage of hydrocyanic acid had been approached only by one Australian plant, viz. *Heterodendron oleaceifolium*, which, in two exceptional samples, had been shown by Petrie<sup>(2)</sup> to yield 0.31 per cent. However, it has since been shown<sup>(3)</sup> that *Eremophila maculata* normally yields under the same conditions up to 0.9 per cent., while Rimington<sup>(4)</sup> has found the South African plant *Dimorphotheca fruticosa* yields 1.5 per cent.

It is not surprising that such a highly cyanogenetic plant should have been suspected of being toxic to animals, although, strangely enough, there is a marked diversity of opinion as to its effect. In "The Poison Plants of Western Australia", 1926, this plant was listed among those suspected of being poisonous, but concerning which we have no definite facts. Maiden<sup>(5)</sup> in 1895, called attention

to its toxicity, but stated that the evidence was contradictory. Ewart, in "Weeds, Poison Plants and Naturalized Aliens in Victoria", 1909, states: "It is often reported as poisonous, but on unsatisfactory evidence. Under ordinary circumstances it is a useful fodder plant on unimproved pastures."

#### HYDROCYANIC ACID IN PLANTS.

It is well known that hydrocyanic acid occurs in a combined state in plants in the form of glucosides. When these are isolated from the plant they are characterised by their great stability, in fact they may be kept for years without change. Contact with their appropriate enzymes, on the other hand, brings about some immediate decomposition, recognisable by the liberation of hydrocyanic acid. Other compounds produced during this decomposition are (1) some kind of sugar, usually glucose, and (2) an unstable intermediate cyanhydrin, composed of hydrocyanic acid with an aldehyde or a ketone. The cyanhydrin readily breaks down into its constituents, either by the action of another enzyme or by the action of heat. Some workers believe that all these products, viz. glucoside, hydrocyanic acid and the intermediate cyanhydrin, are present in the living plant. Others think that normally only glucoside is present, the other substances being produced after injury of the tissues, allowing access of the enzyme to the glucoside. Narishima Acharya<sup>(6)</sup> assumes that in sorghum, for example, there exists what have been termed "labile" compounds which readily yield hydrocyanic acid. We have recently shown that it is quite possible to isolate impure cyanhydrin after allowing emulsin to act on the glucoside of *Phyllanthus Gastroemii*, which contains probably the same constituent as sorghum. This cyanhydrin has the property which has been assigned to the "labile" constituents assumed to be present in sorghum, i.e. it breaks down readily into hydrocyanic acid and aldehyde.

The chief interest of the present work lies in the fact that, although it has not been possible to isolate from or detect a cyanogenetic glucoside of the usual type in this plant, an unstable constituent in an impure form has been obtained which has all the properties of a cyanhydrin. It gives off hydrocyanic acid spontaneously at the ordinary temperature and is readily decomposed by steam. Whether this cyanhydrin is present as such or is a break-down

product of a glucoside is not decided. The experimental evidence points to the former alternative, because the whole of the hydrocyanic acid is removable from the plant by steaming for a few minutes. If it had been produced by enzyme action it is not likely that such action would have proceeded to completion leaving no trace of the original glucoside. The fact that the cyanhydrin is also a phenolic glucoside will be seen on examination of the formula on page 450, but this need not confuse the issue.

In our preliminary observations which were begun under the ægis of the Poison Plants Committee of the C.S.I.R. it was shown that old museum specimens were invariably free from hydrocyanic acid. It was found that this could be accounted for by the fact that when dried by exposure to the air the leaves continuously give off their hydrocyanic acid until, after some months, nearly all has disappeared. In the one sample examined the percentage had fallen in one month from 0.57 to 0.18. It is now shown that in the earlier stages of drying the loss is even more rapid. It is not known exactly how long it takes for the acid to disappear entirely; a sample collected at Coff's Harbour three years ago, when re-examined recently showed a faintly positive reaction for hydrocyanic acid. This point is of interest in view of the question whether it is necessary to take any special precautions in sending specimens of plants for examination for hydrocyanic acid. It will be seen that although quantitative analysis shows a rapid diminution, there is in this case not much likelihood that the whole of the acid will have disappeared before the sample can be examined. It should be emphasized that more unstable materials of this type may yet be found.

The loss of hydrocyanic acid was in the first instance thought to be due to the slow action of the enzyme upon the glucoside during drying. Such a loss is by no means an uncommon phenomenon; it takes place, although at a much slower rate, in the case of *Eucalyptus cladocalyx*, a re-examination of which after some months shows that the acid is still being evolved.<sup>(7)</sup> This explanation, however, did not suffice for the further observation that the acetone extract, which presumably contained no enzyme, also lost hydrocyanic acid continuously, as did also a solid material which was obtained by evaporating and washing the acetone extract. This material was a



yellowish-white solid, readily and almost completely soluble in cold water, reducing Fehling's solution slightly, but freely after boiling its solution with hydrochloric acid, thus revealing its glucosidic character. With phenyl hydrazine hydrochloride it gave a well-defined crystalline compound, melting about 222°. This is described in further detail in the later part of this paper.

These experiments were interrupted at this stage by the resignation of Mr. Cox, and they have only recently been resumed. Specimens of the plant have been supplied by Mr. W. L. Hindmarsh, B.V.Sc., Director of the Veterinary Research Station, Glenfield, and a member of the Poison Plants Committee, and our thanks are due to him and his officers for undertaking this task, which has been more difficult owing to the prevalence of bush fires during the present season.

#### QUALITATIVE EXPERIMENTS WITH THE LEAVES.

When a fresh leaf of a cyanogenetic plant containing enzyme, such as that of peach or cherry laurel, is cut up with scissors and placed in a bottle with a picrate paper under the cork, a positive reaction for hydrocyanic acid is observed in a few minutes. Provided no further injury is inflicted the evolution of hydrocyanic acid soon ceases, and if a fresh picrate paper is substituted after an hour or so, a positive test is no longer obtained. If, however, the experiment is repeated with the leaves of *Goodia lotifolia*, hydrocyanic acid is continuously evolved; in this case it is not even necessary to cut up the leaves.

If a small twig of the living plant be inserted into a bottle without bruising, no sign of hydrocyanic acid is detected, even after 24 hours. A positive reaction is obtained in a few minutes if only one of the small leaves is bruised or cut with scissors.

#### THE ENZYME.

When leaves which have been exposed to the air until practically the whole of the hydrocyanic acid has disappeared are extracted with water and the solution poured into ten times its volume of alcohol, a precipitate is obtained, which after washing has only slight hydrolytic properties when incubated with prunasin or sambunigrin, and none when treated with amygdalin.

## QUANTITATIVE DETERMINATION OF HYDROCYANIC ACID.

In addition to some thirty specimens which have been qualitatively examined since our previous note, all of which have been found to be strongly positive, we have recently examined four larger batches. The method adopted was to macerate with almonds for twenty-four hours, and after steam distillation to titrate with iodine as previously described in this series. The loss of hydrocyanic acid on drying is remarkable.

AMOUNT OF HYDROCYANIC ACID FROM *Goodia lotifolia*.

| Specimen Number. | Collected. | Received. | Analysed             | Percentage of Moisture. | Percentage HCN on Material Dried at 100°. |
|------------------|------------|-----------|----------------------|-------------------------|---|
| 3491             | —          | 15.9.36   | 18.9.36<br>Retested: | 32.0                    | 0.22                                      |
|                  |            |           | 29.9.36              | 8.6                     | 0.2                                       |
| 3503             | 18.9.36    | 22.9.36   | 22.10.36             | 6.4                     | 0.11                                      |
|                  |            |           | 23.9.36              | 59.0                    | 0.86                                      |
|                  |            |           | Retested:            |                         |   |
|                  |            |           | 10.10.36             | 6.5                     | 0.22                                      |
| 3523             | 11.11.36   | 13.11.36  | 13.11.36             | 57.4                    | 0.53                                      |
|                  |            |           | Retested:            |                         |   |
|                  |            |           | 16.11.36             | 6.8                     | 0.30                                      |
|                  |            |           | 23.11.36             |                         | 0.11                                      |
| 3530             | 26.11.36   | 27.11.36  | 27.11.36             | 65.7                    | 0.93                                      |
|                  |            |           | Retested:            |                         |   |
|                  |            |           | 30.11.36             | 8.6                     | 0.22                                      |
|                  |            |           | 1.12.36              | 56.3                    | 0.75                                      |

The first of these samples came from Kempsey, and consisted of leaves, flowers and some small twigs. The latter were separated, and gave 8.5 per cent. of moisture and 0.03 per cent. of hydrocyanic acid. Sample 3530 contained a fair quantity of pods, which gave 21.1 per cent. of moisture and only 0.11 per cent. of acid. The seeds are invariably non-cyanogenetic. Sample 3491, yielding 0.11 per cent., was exposed to the laboratory air for 30 days, and then gave only 0.053 per cent. A similar sample was kept in a closed container in the refrigerator (about 5°) for the same length of time, and showed no loss. The last result for 3530 was obtained from leaves stored in the refrigerator.

EFFECT OF STEAM ON *Goodia lotifolia*.

This plant differs from all others previously examined in yielding the whole of its hydrocyanic acid by distilling

in steam; moreover the greater part of it is removed in ten minutes. Other plants yield a portion only of their acid by such treatment, the quantity obtained being considered a measure of the activity of the enzyme before it has become inactivated by the heat. The following results were obtained. The percentage of hydrocyanic acid was first determined in the usual way after maceration with almonds. Another portion of the weighed material was screwed into a small piece of muslin and thrust down the neck of the distilling flask by means of the steam inlet tube into 100 mls of water previously brought to the boiling point. Steaming was then continued for ten minutes and the receiver was changed. After a further twenty minutes' steaming the contents of the flask were cooled and then macerated with almonds overnight. This gave the hydrocyanic acid from the glucoside which had not been decomposed by steaming or by the original enzyme before its inactivation by the heat. In *Goodia* the hydrocyanic acid obtained by steaming practically represents the whole of that present in the plant. In the other plants examined there are two points to be observed: (1) a much smaller proportion of the acid is obtained by steaming, and (2) the sum of the acid obtained by steaming and that by subsequent hydrolysis of the glucoside is less than the total amount present in the plant. The loss is shown in the last column.

STEAMING EXPERIMENTS WITH *Goodia lotifolia* AND OTHER PLANTS.

|                                       | HCN<br>Present<br>per cent.<br>(on dry). | Steaming<br>10 minutes<br>per cent. | Steaming<br>30 minutes<br>per cent. | HCN<br>After<br>Adding<br>Enzyme<br>per cent. | Loss<br>per cent. |
|---------------------------------------|--|-------------------------------------|-------------------------------------|---|-------------------|
| <i>Goodia lotifolia</i> —             |  |                                     |                                     |   |                   |
| 3523 ground ..                        | 0.30                                     | 93.4                                | 96.2                                | 3.8   | Nil               |
| 3523 minced ..                        | 0.53                                     | 94.3                                | 97.1                                | 2.9   | Nil               |
| 3491 after 30 days'<br>exposure .. .. | 0.06                                     | 64.4                                | 76.3                                | 13.6  | Nil               |
| 3528 .. ..                            | 0.31                                     | 95.5                                | 97.4                                | 2.6   | Nil               |
| 3530 .. ..                            | 0.93                                     | 92.1                                | 94.0                                | 6.0   | Nil               |
| <i>Phyllanthus Gastroemii</i>         | 0.25                                     | 33.7                                | 43.0                                | 16.1  | 40.9              |
| 3529 .. ..                            | 0.32                                     | 19.0                                | 26.0                                | 10.0  | 64.0              |
| *White Clover 3526 ..                 | 0.20                                     | 58.9                                | 64.5                                | 12.7  | 22.8              |
| †Sorghum ( <i>feterita</i> ) ..       | 0.26                                     | 30.0                                | 45.0                                | 10.0  | 45.0              |

\* This sample of New Zealand white clover was kindly supplied by Mr. J. N. Whittet, Government Agrostologist. It was grown in an experimental plot at the Botanical Gardens. It is unusually high in hydrocyanic acid.

† Grown by one of us as a garden plot from seed supplied by Mr. Hindmarsh. Average height, 25 cm.; average weight of plants, 3 grammes.

## EXTRACTION WITH ACETONE.

In order to minimise the decomposition of the cyanogenetic material the ground leaves were allowed to stand in the refrigerator at  $5^{\circ}$  with acetone previously cooled to the same temperature. After two days the acetone solution was filtered and the solvent distilled under reduced pressure, the last traces of the acetone being blown out with the bellows. A deep green extract remained, to which was then added a small quantity of dry ethyl acetate. The whole was then transferred to a beaker and the solid mass kneaded with a spatula until all the green colouring matter was dissolved, and a solid, which felt hard and crystalline, was obtained by suction at the pump. Over a dozen lots of this were made, and all agreed in their general character and behaviour. For convenience this is called material X.

## EXAMINATION OF MATERIAL X.

Material X contained an unstable cyanogenetic substance and at the ordinary temperature began to give off hydrocyanic acid in a few minutes; when heated in a tube placed in boiling water, the acid was immediately recognisable by means of a picrate paper. This material was almost entirely soluble in cold water, very readily soluble in cold methanol or ethyl alcohol, but not very soluble in acetone, nor in ethyl acetate. The watery solution gave a slight reduction when added to boiling Fehling's solution, but a much greater reduction after boiling with hydrochloric acid for a minute. Hydrolysed in this way a red colouration and a precipitate were produced, both of which could be extracted from the acid solution by ethyl acetate with difficulty, but readily by amyl alcohol. With Molisch's reagent a magenta to crimson ring was produced, and a little of the solid gave a crimson colouration when mixed with concentrated sulphuric acid. With phenyl hydrazine hydrochloride a well defined crystalline precipitate was immediately produced. When dissolved in water and the solution steam distilled, the whole of its hydrocyanic acid was removed after about ten minutes, and no more could be obtained on subsequent treatment with sweet almonds. The amount of hydrocyanic acid was determined by titrating the steam distillate with iodine in the usual way. Several batches were thus tested, and gave from 0.6 to 1.3 per cent.

## THE ACTION OF STEAM FOLLOWED BY EMULSIN ON MATERIAL X.

After removing the hydrocyanic acid with steam from two grammes of this material as above described, the liquid in the distilling flask was cooled and shaken with ether, which extracted nothing. The ether was then removed from the aqueous liquid, which was then incubated with powdered sweet almonds for twenty-four hours at 37°. After filtration the liquid was shaken once with petroleum ether to remove any trace of oil and then with ether. This time the ether extracted a colourless crystalline substance which was readily purified by recrystallisation from water. It melted at 116°, and its solution in water gave a purple colouration with ferric chloride. This substance was identified as *p.* hydroxybenzaldehyde, both by the mixed melting point and by that of its phenyl hydrazone. A portion of the liquid after treatment with almonds and extraction with ether was then heated with phenyl hydrazine hydrochloride and sodium acetate for half an hour. An osazone was precipitated which had all the characters of phenyl glucosazone and after recrystallisation from aqueous pyridine melted at 198°–199°.

## THE ACTION OF EMULSIN ON MATERIAL X.

When this material was incubated with almonds as described above, but without the preliminary steam distillation, extraction with ether gave a solid substance containing a cyanhydrin which evolved hydrocyanic acid readily on standing at the ordinary temperature. When this was steam distilled and the aqueous liquid cooled and extracted with ether, *p.* hydroxybenzaldehyde was obtained. The percentage of cyanhydrin was small, amounting to about 3 per cent. A similar product was obtained from the stems and the leaves of the original plant by incubation with almonds and extracting the incubated liquid with ether. That the cyanhydrin of *p.* hydroxybenzaldehyde is not identical with the new cyanhydrin in material X was shown by dissolving some of the latter in water and attempting to extract it with ether. Not a trace of cyanogenetic material was extracted, whereas as shown above and has been previously found in experiments already described, it is quite easy to extract the cyanhydrins of either *m.* or *p.* hydroxybenzaldehyde in this way.

## PHENYLHYDRAZONE FROM MATERIAL X.

Material X gave a phenylhydrazone with the greatest ease. For this purpose seven grammes dissolved in water were freed from its hydrocyanic acid by steam distillation as above described, filtered and cooled. To the solution, measuring 180 mls, a small preliminary quantity of phenylhydrazine hydrochloride was added, in order to carry down any colloidal impurities. After filtration a further quantity of the reagent was added until excess was present. The product crystallised in almost colourless needles. After recrystallisation from slightly diluted alcohol or from methanol it melted at  $230^{\circ}$ .

Analysis: C=60.0, H=6.1 per cent.

$C_{19}H_{22}O_6N_2$  requires C=60.9, H=5.9 per cent.

## HYDROLYSIS OF THE PHENYLHYDRAZONE. ISOLATION OF P. HYDROXY BENZALDEHYDE AND GLUCOSE.

After a preliminary experiment 1 g. of the phenylhydrazone was mixed with 20 mls of 5 per cent. hydrochloric acid and boiled for five minutes, the solid gradually dissolved and the solution became yellow and then brown. On diluting a portion with an equal volume of water a curdy precipitate separated, so a little more hydrochloric acid was added and the heating continued for a few minutes longer. The liquid was then diluted with a little water and extracted with ether several times; the ethereal solution on distillation gave a brownish oil which rapidly solidified. This solid was extracted with hot benzene and the solution filtered from a little brownish solid. On evaporation a slightly yellow solid was obtained which was redissolved in water. On standing in the vacuum desiccator all night a nearly colourless crystalline solid was obtained. Its solution in water gave a purple colour with ferric chloride. It melted at  $115^{\circ}$ , and was recognised as p. hydroxybenzaldehyde by the mixed melting point method.

## Glucose.

After extracting with ether as described above, the strongly acid liquid was neutralised with calcium carbonate, filtered and evaporated on the water bath to about 20 mls. To the liquid was now added one gramme of phenylhydrazine hydrochloride and the same amount of sodium acetate. The slightly turbid liquid was heated in a boiling water bath for about twenty minutes, when a crystalline

yellow precipitate appeared. This had the characteristics of phenyl glucosazone when examined under the microscope. After recrystallisation from aqueous pyridine it melted at 198°.

#### ACETYL DERIVATIVE FROM MATERIAL X.

From the foregoing hydrolysis material X contains the glucoside of p. hydroxybenzaldehyde. So far as we know, this has not been found previously in nature, but has been synthesised by Mauthner.<sup>8</sup>, through its acetyl derivative from the aldehyde and acetobromglucose. Material X readily gave an acetyl compound when boiled for two hours with excess of acetic anhydride in the presence of sodium acetate. After distilling off the excess of acetic anhydride water was added to the reaction mixture in order to decompose the excess of anhydride. On standing overnight the acid solution contained crystals of an acetyl compound, and a further quantity was obtained by boiling with alcohol the syrup which separated from the above acid liquid. The substance readily crystallised from slightly diluted alcohol in either compact crystals or in needles with bayonet-pointed ends. The melting point was 143°. (Mauthner's sample melted at 144° to 145°.)

Analysis: C=55.3, H=5.43 per cent.

$C_{21}H_{24}O_{11}$  requires C=55.7, H=5.3 per cent.

When placed on sulphuric acid a transient pink colouration was produced.

#### ATTEMPT TO SEPARATE THE PURE CYANOGENETIC GLUCOSIDE.

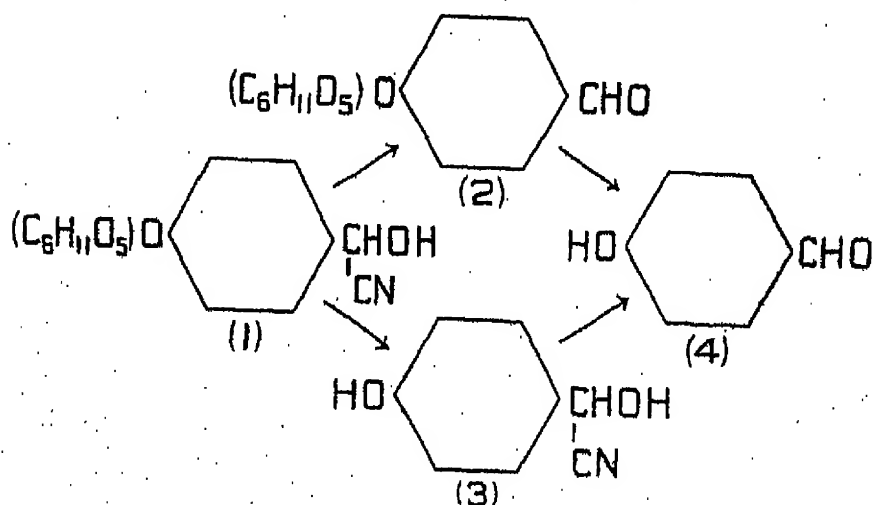
To the deep green ethyl acetate washings from material X about three times the volume of chloroform was added, when a syrup was immediately precipitated. After a few minutes this was washed with dry ethyl acetate to remove a small amount of green mother liquor, when a golden yellow syrup of honey-like consistency was obtained. As much solvent as possible was now removed without heat by the bellows, a weighed quantity transferred immediately to a distilling flask and steam passed through for two periods of ten and fifteen minutes. The amount of hydrocyanic acid, 2.9 per cent., showed that this material was stronger than material X. Over 99 per cent. of the acid distilled in the first ten minute period. Except for the amount of hydrocyanic acid obtained from this

material, there was no qualitative difference between it and material X except that ferric chloride gave a green colour, probably of no significance. When placed in a small tube with a picrate paper there was a positive reaction for hydrocyanic acid in twelve minutes, and after another twenty-four minutes this had become exceedingly marked. When placed in the desiccator overnight a hard glassy mass was obtained, which, when heated with absolute alcohol until a picrate paper no longer gave a positive reaction, assumed the form of rounded particles, but without any sign of crystallisation.

After the separation of the impure material the mixed ethyl acetate and chloroform solution deposited overnight a small quantity of solid material on the sides of the flask. The amount was too small to analyse. It was kept in a small tube with a picrate paper, and by changing the paper it was found to give off hydrocyanic acid continuously for some weeks.

#### SUMMARY.

Although rigid proof is not yet available, the work we have done up to the present points to the conclusion that the unstable cyanogenetic material in *Goodia lotifolia* is the cyanhydrin of the glucoside of p. hydroxybenzaldehyde (1). When this is decomposed by steam distillation or spontaneously, hydrocyanic acid is lost and the phenolic glucoside (2) is formed. With emulsin the latter is converted into p. hydroxybenzaldehyde (4), which can be extracted from the aqueous solution by means of ether, and glucose. On the other hand if emulsin is allowed to act on the cyanhydrin (1) glucose is formed





with an impure, readily extractable cyanhydrin (3), which when decomposed with steam results in the separation of hydrocyanic acid and the formation of p. hydroxybenzaldehyde (4). This can be followed in the scheme on page 450.

#### ACKNOWLEDGMENTS.

Our thanks are due to the Vice-Chancellor of Sydney University for a grant from the Carnegie Research Fund to the Poison Plants Committee of the University and the New South Wales Department of Agriculture. Thanks are also due to Professor C. G. Lambie for facilities for the combustions and to Mr. C. D. Musgrave for the determinations of hydrocyanic acid.

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- (2) Petrie : *Proc. Linn. Soc. N.S.W.*, 1920, 45, 447.
- (3) Finnemore and Cox : *J. Roy. Soc. N.S.W.*, 1930, 73, 172.
- (4) Rimington : *Onderstepoort J. of Vet. Sci. and Animal Ind.*, Vol. 5, No. 1, 1935.
- (5) Maiden : *Agric. Gaz. N.S.W.*, 1895, 6, 306.
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- (8) Mauthner : *J. Prakt. Chem.*, 1912, 85, 564.

Department of Pharmacy,  
University of Sydney.

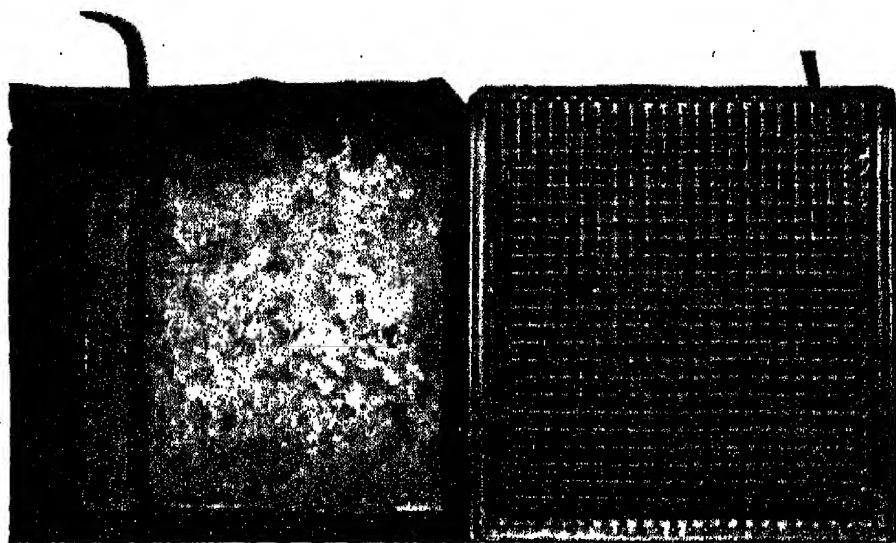
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## THE THERMAL CONDUCTION THROUGH A HOLLOW GLASS BRICK.

By EDGAR H. BOOTH, M.C., D.Sc., F.Inst.P.

*(Manuscript received, February 17, 1937. Read, April 7, 1937.)*

The author was asked to determine the rate at which heat was conducted through a glass brick, which was hollow and of external dimensions 16·5 cms. by 16·5 cms. face and 10 cms. depth, the thickness of the glass walls being about 0·8 cm. The faces were patterned both inside and outside on both fronts so as to prevent direct vision through the blocks, and were constructed in two moulded parts, sealed together by an aluminium solder at 1400° F. (as stated by the manufacturers) so that the hollow was a partial vacuum, being closed at atmospheric pressure at approximately 1100° F. The brick is seen in the accompanying illustrations.



Calculation showed that the rate of transfer of heat from face to face through a system such as this, if completely exhausted in the internal space, would be very low; and it was not considered practicable to estimate the rate of transfer by convection currents through the residual air, and by radiation between the internal faces. A method

had therefore to be devised which would give a measure of the actual rate of transfer, which would be accurate within reasonable limits, yet which would not require unnecessarily elaborate apparatus.

Preliminary tests, using a hot-water bath, electrically maintained at  $100^{\circ}\text{C.}$ , on one face, whilst the other face was maintained at a lower temperature by tap water, showed that the errors introduced by the flow of heat other than through the block were too great, and the method had to be discarded. Consistent results were obtained by the method outlined here.

1. Two containers of rectangular section were constructed of bright galvanised iron, each of internal volume approximately 9 litres. Squares were cut in one face of each of these, on to which the glass brick was placed, a special hard wax being run round so that the line of contact of galvanised iron and glass was watertight. The system then formed a rectangular section "dumb-bell", the link being the glass block, and the ends the two containers. The containers were provided with holes and corks in their tops, from which protruded the ends of stirrers and of long-stem sensitive thermometers; one container also had a larger opening in its top, through which lumps of ice could be introduced later.

A large box, 2 feet  $\times$  2 feet  $\times$  2 feet, was obtained, and strips of linen lint bandages ( $1\frac{1}{2}$  inch section) were nailed to the edges of the open top, so that the "dumb-bell" could be supported in the centre of the box, resting only on the supporting bandages. This was set up in a constant temperature room in the basement of the Physical Laboratories at the University.

One of the containers was filled with water and the other partially filled, and the system was then left until the water had arrived at room temperature. The box was then filled with five pounds of cotton wool, fluffed and teased out, so that the apparatus was very efficiently insulated; the stirrers came partially up through this loose packing, so that they could be manipulated without disturbing it, and the thermometers (reading to  $35^{\circ}\text{C.}$ ) emerged above it; the whole top was then covered with a blanket of cotton wool, in sections, so that by lifting a portion of the blanket temperatures could be read with a minimum of disturbance.

The system was again left so that any temperature change could be noted; in some cases it was left in this state for several hours, in other cases until the following day.

The cotton wool packing was now moved sufficiently at one end to allow lumps of ice to be dropped into that container, and replaced.

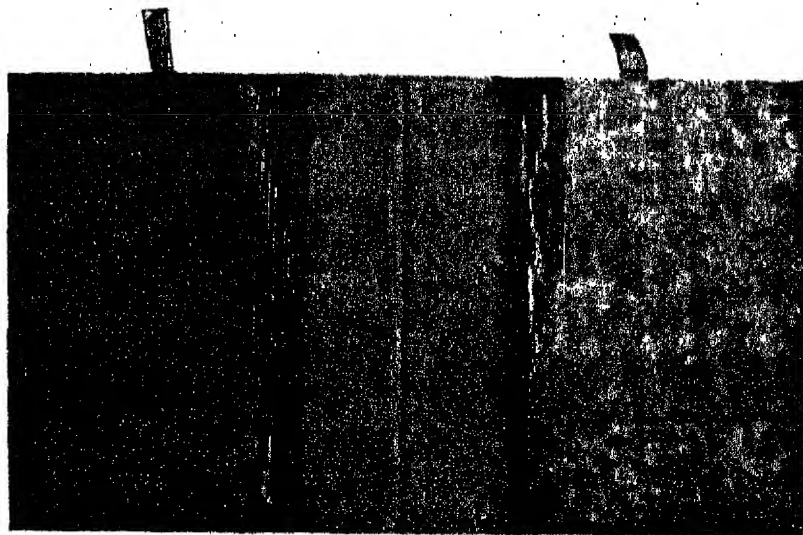
Readings were then taken regularly, the contents of both containers being stirred, and calculations later were based on conditions when the rate of drop in temperature of the water at room temperature became uniform. This drop below the external temperature in the room (the temperature in which changed only slightly during each run) was always very small, so that the gain of heat through the wool to the room temperature water should be quite negligible. There would be a small transfer of heat through the packing from the warmer end to the ice water end, but this is probably negligible within the order of accuracy of the experiment; it would, if of importance, tend to make the stated rate of transfer too high.

Temperatures could be read to  $\frac{1}{20}$ th degree centigrade.

In the experiments as performed, the temperature drop between faces was from about 16° (to 17° C.) down to 0° C.

The rate of transfer of heat through sealed blocks, using this apparatus, was 27 grm. calories per minute for 16 cent. degree difference in temperature of faces, being 1.7 cals./min./cent. deg. per block.

2. To see the effect of the cotton wool packing between the end containers, two bright galvanised iron containers were made of rectangular cross sections of the same size as the glass brick face, on to which the bricks just fitted, being sealed on a line of contact by the special hard wax.



The "dumb-bell" of the previous experiment was thus now replaced by a continuous unit; this is the one illustrated in the figures accompanying this paper. The approximate contents of these containers were  $2\frac{1}{2}$  litres.

The same procedure of support and insulation was adopted as with the first apparatus. The value for sealed bricks was a transfer of 33 grm. calories per minute for 17 cent. degrees difference in temperature of faces, being 1.9 cal./min./cent. deg. per block.

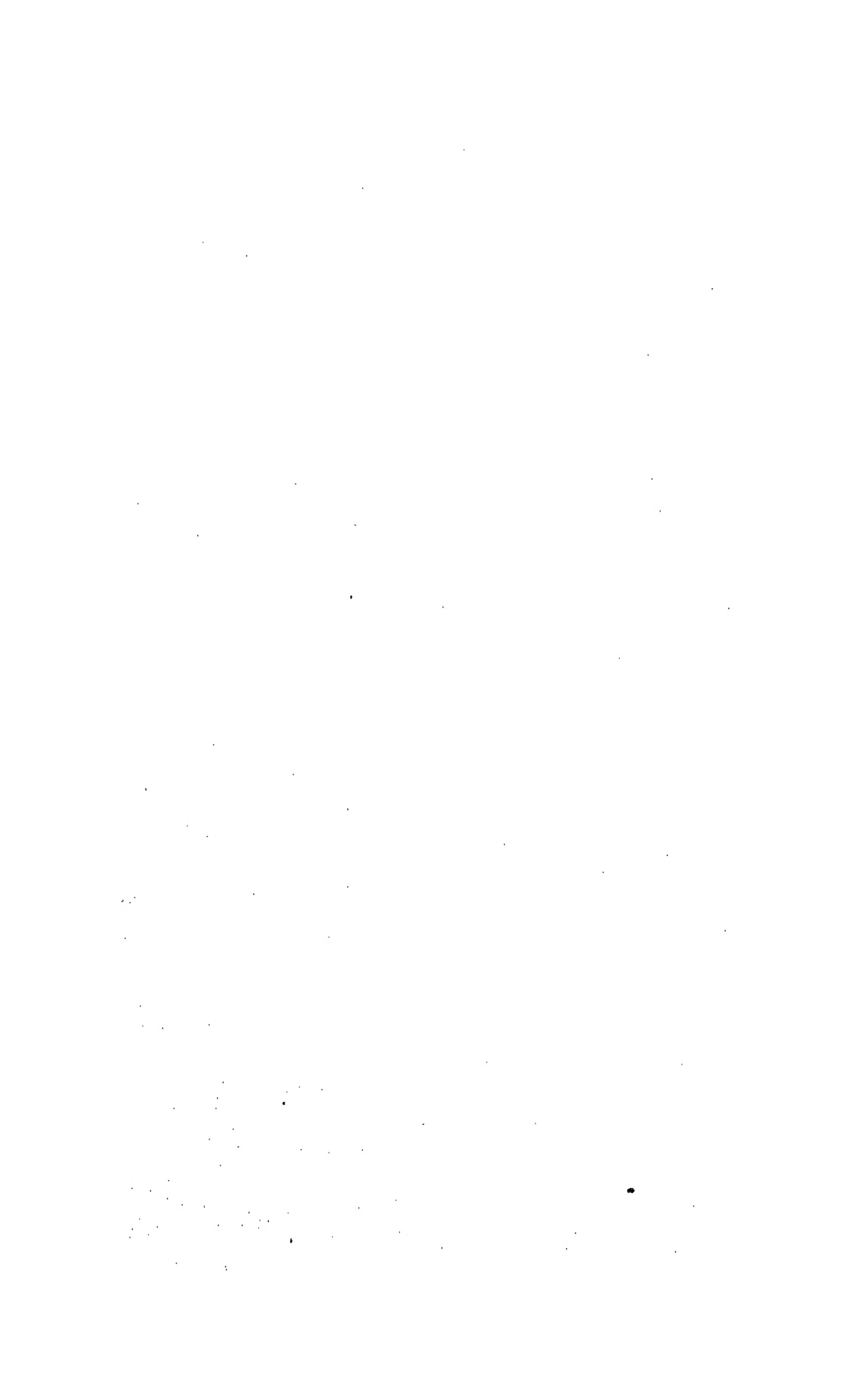
It had been expected that results with this apparatus would have given a lower average than with the other, but these observations are probably within the order of accuracy of the experiments, and of variations in the bricks used.

3. A mean value of 1.8 cal./min./cent. deg. per brick may therefore be taken, neglecting any reducing correction for conduction through the cotton wool. Considering the brick as a single unit, this represents a transfer at the rate of 0.39 grm. cal./sq. cm./hour/cent. deg.

For structural purposes, these bricks are intended to be built up in walls with one-quarter inch mortar joints, and the rate of transfer of energy through such walls (apart from that due to direct radiation transmission) is required. The result, then, based on the observations given above, and stated in British Units, is approximately 0.7 B.T.U./sq. ft. wall face/hour/fah. degree diff. in temp. of opposite faces.

Department of Physics,  
University of Sydney.

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ABSTRACT OF PROCEEDINGS  
OF THE  
**Royal Society of New South Wales**

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*May 6th, 1936.*

The Annual Meeting, being the five hundred and forty-first General Monthly Meeting of the Society, was held in the Hall of Science House, Gloucester and Essex Streets, Sydney, at 7.45 p.m.

Mr. A. R. Penfold, President, was in the chair. Thirty-three members were present. The minutes of the general monthly meeting of the 1st April, 1936, were read and confirmed.

The President announced the deaths of Henry J. W. Brennand, B.A., M.D., Ch.M., V.D., a member since 1891, and of George Inglis Hudson, J.P., F.C.S., a member since 1913.

The certificates of two candidates for admission as ordinary members were read for the first time. The following persons were elected ordinary members of the Society: Edna Maude Goulston, and Harley Weston Wood.

The following gentlemen were elected officers and members of Council for the coming year:

**President:**

MAJOR EDGAR H. BOOTH, M.C., D.Sc., F.Inst.P.

**Vice-Presidents:**

A. R. PENFOLD, F.A.C.I., F.C.S.  
R. J. NOBLE, M.Sc., Ph.D.,  
B.Sc.Agr.

R. W. CHALLINOR, F.I.C., F.C.S.  
W. R. BROWNE, D.Sc.

## Honorary Secretaries :

C. A. SUSSMILCH, F.G.S.

| C. ANDERSON, M.A., D.Sc.

## Honorary Treasurer :

EDWIN CHEEL.

## Members of Council :

PROF. L. A. COTTON, M.A., D.Sc.  
 PROF. J. C. EARL, D.Sc., Ph.D.  
 PROF. A. P. ELKIN, M.A., Ph.D.  
 H. FINNEMORE, B.Sc., F.I.C.  
 D. P. MELLOR, M.Sc.  
 Assoc.-PROF. H. PRIESTLEY,  
 M.D., Ch.M.

PROF. J. DOUGLAS STEWART,  
 B.V.Sc., F.R.C.V.S.  
 L. L. WATERHOUSE, B.E.  
 W. L. WATERHOUSE, M.C.,  
 D.Sc.Agr., D.I.C.  
 M. B. WELCH, B.Sc., A.I.C.

The Annual Balance Sheet and Revenue Account were submitted to members by the Honorary Treasurer. Mr. Clunies Ross congratulated the Council on the present satisfactory state of the Society's finances, and on the clear presentation of the position. On the motion of Mr. Cheel, seconded by Mr. Ollé, the Balance Sheet and Revenue Account were adopted.

## ROYAL SOCIETY OF NEW SOUTH WALES.

## BALANCE SHEET AS AT 31st MARCH, 1936.

## LIABILITIES.

| 1935.          |                               | 1936. |    |    |                     |
|----------------|-------------------------------|-------|----|----|---------------------|
| £              |                               | £     | s. | d. | £ s. d.             |
|                | Trust Funds—                  |       |    |    |                     |
|                | Clarke Memorial Fund          | 1,660 | 1  | 8  |                     |
|                | Walter Burfitt Prizo          |       |    |    |                     |
|                | Fund .. .. .                  | 613   | 17 | 2  |                     |
|                | Liversidge Bequest ..         | 603   | 5  | 7  |                     |
| 2,825          |                               |       |    |    | 2,877 4 5           |
|                | Subscriptions Paid in Advance |       |    |    | 59 17 0             |
| 16             | Sundry Liabilities .. ..      |       |    |    |                     |
|                | Provision for Unexpired Pro-  |       |    |    |                     |
|                | portion of Life Member-       |       |    |    |                     |
|                | ship Subscriptions ..         |       |    |    | 150 0 0             |
| 30,563         | Accumulated Funds ..          |       |    |    | 26,016 13 2         |
| <u>£33,404</u> |                               |       |    |    | <u>£29,103 14 7</u> |



# ABSTRACT OF PROCEEDINGS.

xxix

## ASSETS.

| 1935.   |                           |            | 1936. |         |       |
|---------|---------------------------|------------|-------|---------|-------|
| £       |                           |            | £     | s.      | d.    |
|         | Cash at Bank and on Hand— |            |       |         |       |
|         | Union Bank of Australia   |            |       |         |       |
|         | Ltd. .. ..                | 370 7 11   |       |         |       |
|         | Commonwealth Savings      |            |       |         |       |
|         | Bank .. ..                | 220 0 0    |       |         |       |
|         | Petty Cash .. ..          | 0 8 11     |       |         |       |
| 461     |                           |            |       | 590     | 16 10 |
|         | Commonwealth Bonds and    |            |       |         |       |
|         | Inscribed Stock—          |            |       |         |       |
|         | Bonds (Nominal value      |            |       |         |       |
|         | £4,340) .. ..             | 4,291 10 0 |       |         |       |
|         | Stock (Nominal value      |            |       |         |       |
|         | £1,000) .. ..             | 990 10 0   |       |         |       |
| 4,080   |                           |            |       | 5,282   | 0 0   |
|         | Science House Management  |            |       |         |       |
|         | Committee—                |            |       |         |       |
| 14,534  | Payments to date ..       |            |       | 14,540  | 0 0   |
|         | Sundry Debtors—           |            |       |         |       |
|         | Institution of Engineers  | 1,283 6 8  |       |         |       |
|         | Sundries .. ..            | 1 2 5      |       |         |       |
|         | Subscriptions             |            |       |         |       |
|         | Unpaid £525 17 6          |            |       |         |       |
|         | Less Reserve 466 19 4     |            |       |         |       |
|         |                           | 58 18 2    |       |         |       |
| 2,461   |                           |            |       | 1,343   | 7 3   |
| 9,979   | Library .. ..             |            |       | 6,800   | 0 0   |
| 1,583   | Furniture .. ..           |            |       | 450     | 5 6   |
| 162     | Pictures .. ..            |            |       | 53      | 10 0  |
| 108     | Microscopes .. ..         |            |       | 23      | 15 0  |
| 36      | Lantern .. ..             |            |       | 20      | 0 0   |
| £33,404 |                           |            |       | £29,103 | 14 7  |

The above Balance Sheet has been prepared from the books, accounts and vouchers of the Royal Society of New South Wales, and is a correct statement of the position of the Society's affairs on the 31st March, 1936, as disclosed thereby. We have a certificate from the Union Bank of Australia Limited that they hold Commonwealth Bonds to a nominal value of £4,340 on behalf of the Society, and a certificate from the Registrar of Inscribed Stock that stock to the nominal value of £1,000 is inscribed in the name of the Society.

HORLEY & HORLEY,

Per CONRAD F. HORLEY, F.A.A.,  
Public Accountants, Auditors.

(Sgd.) EDWIN CHEEL,  
Honorary Treasurer.

National Mutual Building,  
350 George Street,  
Sydney, 28th April, 1936.

**REVENUE ACCOUNT FOR THE YEAR ENDED  
31st MARCH, 1936.**

| Year ended<br>31st March,<br>1935. |   |     | Year ended<br>31st March, 1936. |             |
|------------------------------------|---|-----|---------------------------------|-------------|
| £                                  |   |     | £                               | s. d.       |
| 3                                  | To Advertising .. ..  | 2   | 5                               | 3           |
| 21                                 | „ Cleaning .. ..  | 25  | 10                              | 0           |
| 6                                  | „ Electric Light and Gas ..   | 2   | 18                              | 10          |
| 22                                 | „ Insurance .. ..   | 21  | 11                              | 10          |
| 65                                 | „ Miscellaneous Expenses ..   | 64  | 3                               | 8           |
| 278                                | „ Office Salaries and Audit Fees  | 249 | 0                               | 8           |
| 43                                 | „ Office Sundries and Stationery  | 20  | 5                               | 6           |
| 58                                 | „ Printing .. ..  | 116 | 5                               | 0           |
|                                    | „ Printing and Publishing   |     |                                 |             |
| 229                                | Journal .. ..   | 280 | 4                               | 8           |
| 51                                 | „ Stamps and Telegrams ..   | 60  | 0                               | 0           |
| 15                                 | „ Telephone .. ..   | 16  | 15                              | 4           |
| 208                                | „ Depreciation .. ..  | —   |                                 |             |
|                                    | „ Annual Dinner—  |     |                                 |             |
|                                    | Expenses £63 15 11  |     |                                 |             |
|                                    | Less Received 53 0 6  |     |                                 |             |
|                                    |   | 10  | 15                              | 5           |
|                                    | „ Conversazione—  |     |                                 |             |
|                                    | Expenses £7 4 7   |     |                                 |             |
|                                    | Less Received 5 2 0   |     |                                 |             |
|                                    |   | 2   | 2                               | 7           |
|                                    |   |     | 871                             | 18 9        |
| 88                                 | „ Balance, being Net Revenue<br>for the year, transferred to<br>Accumulated Fund .. |     | 187                             | 14 9        |
| <u>£1,087</u>                      |   |     | <u>£1,059</u>                   | <u>13 6</u> |

| Year ended<br>31st March,<br>1935. |   |                             | Year ended<br>31st March, 1936. |             |
|------------------------------------|---|-----------------------------|---------------------------------|-------------|
| £                                  | £   |                             | £                               | s. d.       |
| 546                                | By Members' Subscriptions ..              | 546                         | 0                               | 0           |
| 200                                | „ Government Subsidy ..                   | 275                         | 0                               | 0           |
| 270                                | „ Science House Receipts ..               | 220                         | 0                               | 0           |
| 232                                | Less Rent Paid ..                         | 199                         | 15                              | 3           |
|                                    |   |                             |                                 |             |
|                                    | 38  |                             | 20                              | 4 9         |
|                                    | 96  | „ Miscellaneous Receipts .. | 75                              | 10 6        |
| 322                                | „ Interest Received ..                    | 255                         | 18                              | 0           |
|                                    | Less—                                     |                             |                                 |             |
|                                    | Clarke Memorial<br>Fund £64 3 6           |                             |                                 |             |
|                                    | Walter Bur-<br>fitt Prize<br>Fund 25 12 2 |                             |                                 |             |
|                                    | Liversidge<br>Bequest 23 4 1              |                             |                                 |             |
| 115                                |   | 112                         | 19                              | 9           |
| <u>207</u>                         |   |                             | 142                             | 18 3        |
| <u>£1,087</u>                      |   |                             | <u>£1,059</u>                   | <u>13 6</u> |

**ACCUMULATED FUND ACCOUNT FOR THE YEAR  
ENDED 31st MARCH, 1936.**

| 1936—March 31—  | £   | s. | d. | £              | s.        | d.       |
|---|-----|----|----|----------------|-----------|----------|
| To Adjustment on Valuation of Library,<br>Furniture, Pictures, Microscopes<br>and Lantern .. .. . |     |    |    | 4,634          | 12        | 0        |
| „ Adjustment of Subscriptions to agree<br>with Register of Members ..                             | 4   | 4  | 0  |                |           |          |
| „ Arrears of Subscription, written off  | 107 | 10 | 0  |                |           |          |
|   |     |    |    | 111            | 14        | 0        |
| „ Provision for Life Members ..   |     |    |    | 150            | 0         | 0        |
| „ Balance Carried Down .. ..  |     |    |    | 26,016         | 13        | 2        |
|   |     |    |    | <u>£30,912</u> | <u>19</u> | <u>2</u> |

| 1935—March 31—    | £      | s. | d. |
|-------------------|--------|----|----|
| By Balance.. .. . | 30,562 | 16 | 5  |

| 1936—March 31—   | £              | s.        | d.       |
|--|----------------|-----------|----------|
| By Amount Capitalised by Science House Management<br>Committee .. .. . | 6              | 1         | 8        |
| „ Amount Received from Estate H. G. Chapman                            | 114            | 6         | 4        |
| „ Life Membership Fees .. .. .   | 42             | 0         | 0        |
| „ Net Revenue for the Year .. .. .                                     | 187            | 14        | 9        |
|  | <u>£30,912</u> | <u>19</u> | <u>2</u> |

| 1936—March 31—    | £       | s. | d. |
|-------------------|---------|----|----|
| By Balance.. .. . | £26,016 | 13 | 2  |

Major Booth proposed and Professor Watt seconded, that Mr. C. F. Horley, F.A.A., of Messrs. Horley & Horley, public accountants, should be appointed the Society's auditor for the year 1936-37. This was the only nomination received, and Mr. Horley was declared elected.

The Annual Report of the Council (1935-1936) was read, and on the motion of Major Booth, seconded by Mr. Cheel, was adopted.

**REPORT OF THE COUNCIL FOR THE YEAR 1935-36.**

(1st May to 29th April.)

We regret to report that we have lost by death six ordinary members. By resignation we have lost ten members, and, in addition, eight members have been struck off the roll for non-payment of subscriptions. On the other hand, forty-eight ordinary members and one honorary member have been elected. Today (29th April, 1936) the roll of members stands at 296.

During the Society's year there have been nine general meetings and eleven council meetings. The average attendance has been 39 at general meetings and 15 at council meetings.

Nineteen papers were read at the general monthly meetings, and covered the usual wide range of subjects. In 1936, for the first time, a monthly meeting was held in April; three papers were read, a demonstration and a lecturette were given, and the meeting was well attended.

The following short talks on current topics were delivered at general meetings during the year:

"Chemical Warfare", by H. Finnemore, B.Sc., F.I.C.

"Aerogels", by D. P. Mellor, M.Sc.

"Plant Genetics", by Edwin Cheel.

"Ergot in Paspalum", by R. J. Noble, M.Sc., Ph.D., B.Sc.Agr.

At two meetings in the year a symposium was held, the subjects of discussion and the speakers being as follows:

3rd July: "Sulphur." Speakers: Professors L. A. Cotton and R. D. Watt, and Mr. J. C. Firth. In the absence of Mr. R. F. Boan, his contribution was read by the President.

6th November: "A Discussion on the Upper Atmosphere." Speakers: Dr. D. F. Martyn, Professor O. U. Vonwiller, Dr. T. Iredale, Professor V. A. Bailey, Dr. J. E. Mills and Mr. G. H. Godfrey.

Four Popular Science Lectures were given, as follows:

18th July: "Recent Advances in Veterinary Research in Australia", by Dr. H. R. Carne.

15th August: "Giants or Dwarfs: Studies of Growth in Human Beings", by Professor Harvey Sutton.

19th September: "Measuring the Stars", by Rev. W. J. O'Leary.

17th October: "Volcanoes of the Pacific", by Mr. C. A. Sussmilleh.

The Annual Dinner was held on Thursday, the 23rd April, 1936, in David Jones' Auditorium; 110 persons were present.

In August, 1935, a *Conversazione* was held in Science House, Dr. H. Brose being the principal guest. On 13th March, 1936, the Society participated in a joint meeting with other scientific societies at the University to celebrate the 100th anniversary of Charles Darwin's visit to Australia.

In October, 1935, Dr. Browne resigned his position as Honorary Secretary and Editor of the "Journal and Proceedings". Dr. C. Anderson was elected as Honorary Secretary in Dr. Browne's place, and Dr. Browne was elected a member of Council to fill the vacancy caused by the election of Dr. Anderson as Honorary Secretary. The Council placed on record their appreciation of Dr. Browne's services as Honorary Secretary.

At the Annual General Meeting held in May, 1935, various alterations to the rules were ratified by the members. The rules relating to membership having been altered to allow the Council to elect to honorary life membership members of more than forty years' standing, the following five persons were elected life members: W. H. Crago, F. Poate, G. R. Cowdery, G. H. Halligan, and R. T. McKay.

During 1935 the Council obtained legal advice as to the eligibility of women as members of the Society, and it was found that nothing in the rules precluded their election. There are now eleven women members.

The third award of the Walter Burfitt Prize and Medal was made in November, 1935, to Associate-Professor Victor Albert Bailey, M.A.,

D.Phil., for his research work in Physics, Radio, and the application of mathematical and statistical methods in Biology.

During the year a Clarke Memorial Fund Permanent Advisory Committee was appointed by the Council, and, on its recommendation, Dr. W. G. Woolnough was asked to deliver a "Clarke Memorial Lecture". This lecture was delivered on the 20th March, 1936, the title being "The Aeroplane in the Service of Geology".

The Clarke Memorial Medal for 1936 was awarded to Sir Douglas Mawson, Kt., O.B.E., F.R.S., D.Sc., B.E.

*Science House.*—Meetings of the Science House Joint Management Committee, at which the Royal Society has been regularly represented, have been held throughout the year. A Common Room has been furnished and set aside for the use of the members of the tenant bodies.

*The Library.*—Two Honorary Librarians, Professor J. C. Earl and Mr. H. Williams, were appointed by the Council, and the following Library Committee was elected: the Executive Officers, the Honorary Librarians, Professor C. E. Fawsitt, Dr. C. Anderson, and Mr. C. A. Sussmilch. One meeting of the Library Committee was held during the year.

During the year ending 31st March, 1936, 4,011 parts of periodicals and 329 volumes have been received. Of these, 1,604 issues have been back numbers; this means that a large number of the Library's sets have been made more nearly complete. An increase of approximately 10% in the total number of publications received has been recorded.

The number of visitors to the library has increased in a very satisfactory manner from 78 for the year ending 31st March, 1935, to 183 for the year ending 31st March, 1936, an increase of 134%. The experiment of opening the library until 7.45 p.m. on the evenings of the general monthly meetings was tried during the past year, but with a disappointing result. Brief notices, calling members' attention to library regulations, important gifts, etc., have appeared on the monthly circulars for the past six months.

The Council made a grant of £50 each for binding and purchase of periodicals, and the amounts spent were:

|                       |    |    |      |    |   |
|-----------------------|----|----|------|----|---|
| Books and periodicals | .. | .. | £54  | 11 | 6 |
| Binding .. .. .       | .. | .. | 47   | 12 | 0 |
|                       |    |    | £102 | 3  | 6 |

Some changes in the exchange list have been made, and the total number of institutions to which the "Journal and Proceedings" is sent is now 343.

In August, 1935, 500 copies of a List of Periodicals Received Regularly by the Society's Library were printed, and about 350 copies have been distributed. The cost of printing a complete catalogue of the library was too great for the Council to consider, and the publication of this list, which contains some 500 names of publications, has served a useful purpose in making the contents of the library more widely known among the members, all of whom cannot have easy access to Pitt's Catalogue of Scientific Periodicals, in which a complete list of the library's contents may be found. (This Catalogue is shortly to be revised, and a large number of alterations in the Society's entries will then be made.)

The Council purchased a vacuum cleaner for use in the library, and the cleaning of the library is steadily progressing. A change in the staff was made in December, 1935, and an office and library assistant

has been employed for mornings only. This arrangement is only temporary.

Holland blinds have been purchased and fixed to the windows on the west side of the library, in order to prevent any further damage being done by the sun to books on the shelves near these windows.

The reciprocal arrangements anticipated with the Linnean Society and The Institution of Engineers have not yet been made. The Societies named have in the past been willing to allow accredited persons to use their libraries, and have given this privilege to members of the Royal Society.

On behalf of the Council,  
A. R. PENFOLD,  
President.

The President announced that the following Popular Science Lectures would be delivered during the year :

16th July : " Soil Erosion and the Use of the Land ", by Professor J. Macdonald Holmes.

20th August : " Bacteria in Relation to Industry ", by E. G. Pont, M.Sc.Agr.

17th September : " X-rays and Radium Treatment of Cancer ", by Dr. W. H. Love.

15th October : " Silk, Satin, Cotton, Rags. The origin of certain natural and artificial textiles ", by Professor J. C. Earl.

The following donations were received : 139 parts of periodicals and 8 whole volumes.

The Honorary Secretary read a letter from the Official Secretary to the Governor-General, stating that His Excellency Lord Gowrie is pleased to grant his patronage to the Society during his period of office as Governor-General.

The President, Mr. A. R. Penfold, delivered his address, entitled " The Present Position of the Forest Products in Australia ".

Mr. Penfold, the retiring President, then installed Major Edgar H. Booth as President for the year 1936-37, and the latter briefly returned thanks. Major Booth then, on behalf of the Council and of members of the Society, congratulated the retiring President on the presentation of his address, and thanked him for his valuable and continuous services in the interests of the Society throughout his term of office.

*June 3, 1936.*

The five hundred and forty-second General Monthly Meeting was held in the Hall of Science House, Gloucester Street, at 7.45 p.m.

Major E. H. Booth, President, was in the chair. Thirty-five members and visitors were present. The minutes of the general monthly and annual meeting of the 6th May, 1936, were read and confirmed.

The President announced the death of Charles Walker F.C.S., A.A.C.I., who had been a member since 1910.

The certificates of three candidates for admission as ordinary members of the Society were read, one for the first, and two for the second time. The following persons were duly elected ordinary members of the Society: Mrs. Kathleen Margaret Maria Sherrard, and Ernest Lee Walter.

The following donations were received: 341 parts of periodicals and 31 whole volumes.

The following papers were read:

"The Upper Palaeozoic Rocks around Yessabah, near Kempsey", by A. H. Voisey, B.Sc.

"Compounds formed by Mercury Salts with Tertiary Arsines", by J. J. Anderson, B.Sc., and G. J. Burrows, B.Sc.

"The Ben Bullen Plutonic Complex, N.S.W.", by Germaine A. Joplin, B.Sc., Ph.D.

"Cyanogenetic Glucosides in Australian Plants. Part 4. *Zieria laevigata*", by H. Finnemore, B.Sc., F.I.C., and Joyce M. Cooper, B.Sc.

"An Attempt at Quantitative Analysis of Silver-Gold Alloys by Optical Spectroscopy", by Winifred Mankin, M.Sc. (Communicated by Professor O. U. Vonwiller.)

"Geology of North-West Basin, Western Australia, with particular reference to the stratigraphy of the Permo-carboniferous", by H. G. Raggatt, M.Sc.

*July 1st, 1936.*

The five hundred and forty-third General Monthly Meeting was held in the Hall of Science House, Gloucester Street, at 7.45 p.m.

Major E. H. Booth, President, was in the chair. Thirty-eight members were present. The minutes of the preceding meeting were read and confirmed.

The certificates of three candidates for admission as ordinary members of the Society were read, two for the first, and one for the second time. Max Rudolf Lemberg was duly elected an ordinary member of the Society.

The President announced that it had been decided by the Royal Society, and other scientific organisations, to call for subscriptions to a fund, the object of which would be to obtain a portrait of the late Sir Edgeworth David, to be hung in the Hall of Science House.

The following donations were received: 252 parts of periodicals and 32 whole volumes.

The following paper was read:

"The Optical Properties and Crystal Structure of Some Compounds of the Type  $R_xMX_4$ ", by D. P. Mellor, M.Sc., and F. M. Quodling, B.Sc.

Mr. C. A. Sussmilch delivered a lecturette, entitled "A Geographical Excursion to Eastern Queensland".

Mr. D. P. Mellor made two exhibits, of "Heavy Water", and of "A new type of polarising screens". Mr. H. H. Baker exhibited an "Audiometer".

*August 5th, 1936.*

The five hundred and forty-fourth General Monthly Meeting was held in the Hall of Science House, Gloucester Street, at 7.45 p.m.

Major E. H. Booth, President, was in the chair. Twenty-five members and visitors were present. The minutes of the preceding meeting were read and confirmed.

The President announced the death of Sir Albert Gould, K.B., V.D., a member since 1897.

The certificates of two candidates for admission as ordinary members of the Society were read for the second time, and the following gentlemen were duly elected ordinary members of the Society: Arthur Frederick Alan Harper, and Edward Eugene Hirst.

The following donations were received: 248 parts of periodicals and 31 whole volumes.

The following papers were read:

"Co-ordination Compounds of Cadmium with Tertiary Arsines", by G. J. Burrows, B.Sc., and A. Lench, B.Sc.

"Derivatives of Zinc Halides with Tertiary Arsines", by G. J. Burrows, B.Sc., and A. Lench, B.Sc.

"The Reaction of Creatinine with 1, 3, 5-Trinitrobenzol, 2, 4, 6-Trinitrotoluol, and 2, 4, 6-Trinitrobenzoic Acid", by A. Bolliger, Ph.D.

"The Causes of Ice Ages", by G. H. Halligan, F.G.S.

"Cyanogenetic Glucosides in Australian Plants. Part 5. *Phyllanthus gastroemii*", by H. Finnemore, B.Sc., Suzanne K. Reichard, B.Sc., and Dorothy K. Large, B.Sc.

*September 2nd, 1936.*

The five hundred and forty-fifth General Monthly Meeting was held in the Hall of Science House, Gloucester Street, at 7.45 p.m.



Major E. H. Booth, President, was in the chair. Twenty-six members were present. The minutes of the preceding meeting were read and confirmed.

The President announced the deaths of Robert Newby Kirk, a member since 1919, and of Charles Dudley Ryder, D.Eng. (*Vienna*), Assoc.I.R.S.M. (*Lond.*), A.A.C.I., F.C.S., a member since 1907.

The following donations were received: 300 parts of periodicals and 25 whole volumes.

The Honorary Secretary read a letter from the private secretary to His Excellency the Governor, informing the Society of His Excellency's acceptance of the office of Vice-Patron.

The following papers were read:

"Evidence of a change of sea-level at Botany Bay", by C. A. Sussmilch.

"A Study of Phosphate Solubility in Certain N.S.W. Soils", by W. M. Holman, B.Sc.Agr. (Communicated by Professor R. D. Watt.)

Mr. A. R. Penfold gave a short talk, entitled "Some Recent Developments in Plastics"; he also exhibited a number of articles made of the materials of which he was speaking.

Mr. E. G. Bishop made an exhibit of "sub-standard gauges".

*October 7th, 1936.*

The five hundred and forty-sixth General Monthly Meeting was held in the Hall of Science House, Gloucester Street, at 7.45 p.m.

Major E. H. Booth, President, was in the chair. Thirty-four members and visitors were present. The minutes of the preceding meeting were read and confirmed.

The certificate of a candidate for admission as an ordinary member of the Society was read for the first time.

The following donations were received: 250 parts of periodicals and 16 whole volumes.

The following papers were read:

"Some Notes on the Physiography of the Lake George Region, with special reference to the origin of Lake George", by M. D. Garretty, B.Sc.

"The Action of Lead Tetrachloride on Primary and Secondary Halogenated Arsines and on Tertiary Arsines", by G. J. Burrows, B.Sc., and A. Lench, B.Sc.

- "Note. Diphenyl Dihydroxy Arsonium Chloride,  $\text{Ph}_2\text{As}(\text{OH})_2\text{Cl}$ ",  
by G. J. Burrows, B.Sc., and A. Lench, B.Sc.  
"Interference by Reflexion from a Concave Spherical Mirror",  
by O. U. Vonwiller, B.Sc., F.Inst.P.  
"The Action of Nitrous Acid on Amines", by J. C. Earl, D.Sc.,  
Ph.D., and N. G. Hills, B.Sc.

*November 4th, 1936.*

The five hundred and forty-seventh General Monthly Meeting was held in the Hall of Science House, Gloucester Street, at 7.45 p.m.

Major E. H. Booth, President, was in the chair. Forty-two members and visitors were present. The minutes of the preceding meeting were read and confirmed.

The President announced the death of Albert John Fortescue, a member since 1920.

The certificate of a candidate for admission as an ordinary member of the Society was read for the second time, and Cecil Scott Waine was duly elected a member.

The following donations were received: 182 parts of periodicals and 15 whole volumes.

The following papers were read:

- "Evidence of Magmatic Stopping in a Dyke at Hartley, N.S.W.",  
by Alma G. Culey, M.Sc., and Germaine A. Joplin, B.Sc.,  
Ph.D.  
"The Electrode Potential of Thin Films of Zinc on Platinum",  
by D. P. Mellor, M.Sc., and H. Mulhall.  
"Some Observations of Zonal Discordance in Diurnal Magnetic  
Variations", by Edgar H. Booth, M.C., D.Sc., F.Inst.P.  
"Some Observations on the Occurrence of Bile Pigment Hæmo-  
chromogens in Nature and on their formation from Hæmatin  
and Hæmoglobin", by R. Lemberg and R. A. Wyndham.  
"On the Chemistry of Jaffe's Reaction for Creatinine", by A.  
Bolliger, Ph.D.  
"Geological Notes on the Country between the Yass and Shoal-  
haven Rivers", by M. D. Garretty, B.Sc.

*December 2nd, 1936.*

The five hundred and forty-eighth General Monthly Meeting was held in the Hall of Science House, Gloucester Street, at 7.45 p.m.

Major E. H. Booth, President, was in the chair. Thirty-one members were present. The minutes of the preceding meeting were read and confirmed.

The certificate of a candidate for admission as an ordinary member of the Society was read for the first time.

The following donations were received: 221 parts of periodicals and 19 whole volumes.

The following papers were read :

- "The Occurrence of a number of varieties of *Eucalyptus radiata* (*E. numerosa*) as Determined by Chemical Analyses of the Essential Oils. Part II", by A. R. Penfold, F.A.C.I., F.C.S., and F. R. Morrison, A.A.C.I., F.C.S.
- "Species of *Helminthosporium* and *Curvularia* associated with Root-rot of wheat and other graminaceous plants", by H. J. Hynes, D.Sc.Agr., M.Sc.
- "Energy Distributions in the Spectra of Some Gaseous Discharge Tubes", by R. G. Giovanelli. (Communicated by Professor O. U. Vonwiller.)
- "Probable Late Silurian Age of Serpentine, Condobolin-Trundle District, N.S.W.", by H. G. Raggatt, M.Sc.
- "Some Derivatives of Diphenyl Methyl Arsine", by G. J. Burrows, B.Sc., and A. Lench, B.Sc.
- "Cyanogenetic Glucosides in Australian Plants. Part 6. *Goodia lotifolia*, an unstable constituent", by H. Finnemore, B.Sc., F.I.C., and Dorothy K. Large, B.Sc.
- "N-phenyl Pyrroles derived from Phenacyl laevulinic acid", by Muriel G. Holdsworth, M.Sc., and Francis Lions, B.Sc., Ph.D.
- "Some Derivatives of 3-n-Propyl-phenol", by S. G. Cousin, B.Sc., and Francis Lions, B.Sc., Ph.D.
- "Nicotinyln Morpholine", by Rita H. Harradence, and Francis Lions, B.Sc., Ph.D.
- "Morpholine as a Reagent for Mobile Halogen Atoms and Nitro-Groups", by Rita H. Harradence and Francis Lions, B.Sc., Ph.D.

The last six papers were read by title only.

Before the conclusion of the meeting the President wished the members the compliments of the season.

*April 7th, 1937.*

The five hundred and forty-ninth General Monthly Meeting was held in the Hall of Science House, Gloucester Street, at 7.45 p.m.

Major E. H. Booth, President, was in the chair. Forty members were present. The minutes of the preceding meeting were read and confirmed.

The President announced the deaths of Ernest Lee Walter, a member since 1936, Charles Mylne McDonald, a member since 1935, Guillaume Daniel Delprat, a member since 1921, Walter L. Hammond, a member since 1909, and Sir Grafton Elliot Smith, an honorary member since 1928.

The certificates of two candidates for admission as ordinary members of the Society were read, one for the first, and one for the second time. The following gentleman was duly elected an ordinary member of the Society: Fritz Reuter.

The President announced that the Clarke Memorial Lecture for 1937 would be delivered on the 19th April, by Professor H. C. Richards, the title being "The Great Barrier Reef of Australia, and its Origin".

The following donations were received: 988 parts of periodicals and 51 whole volumes.

The following paper was read:

"The Thermal Conduction through a Hollow Glass Brick", by Edgar H. Booth, M.C., D.Sc., F.Inst.P.

Major Booth then delivered a short talk, entitled "The A.N.Z.A.A.S. Meeting in New Zealand", and illustrated this with moving pictures. Messrs. A. R. Penfold and E. C. Andrews also spoke on this subject.

An exhibit of "Cosmic Ray Tracks" was shown by Professor O. U. Vonwiller.

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ABSTRACT OF PROCEEDINGS  
OF THE SECTION OF  
**INDUSTRY**

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OFFICERS :

*Chairman :* A. D. Ollé, F.C.S., A.A.C.I.

*Hon. Secretary :* E. G. Bishop.

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Eight afternoon visits were arranged during the year 1936-37 to various industrial, commercial and other establishments around Sydney. The trouble that was taken in every case by the management to provide guides and explain their processes made these visits of great interest to the members of the Section. The following places were visited :

Tuesday, 12th May.—Gas Appliance Testing and Research Laboratories of The Australian Gas Light Company, Camperdown.

Tuesday, 9th June.—Australian Window Glass Pty. Ltd., Alexandria.

Tuesday, 14th July.—*Sun* Newspapers Ltd., Sydney.

Tuesday, 11th August.—Ford Motor Company, Homebush.

Tuesday, 8th September.—Joyce Biscuits Ltd., Camperdown.

Tuesday, 13th October.—Exide Battery Company, Leichhardt.

Tuesday, 10th November.—Laboratories of Parke, Davis & Co., Rosebery.

Tuesday, 13th April.—Farmer & Company Ltd., Sydney, to inspect Carrier Air-Conditioning Plant.

# ABSTRACT OF PROCEEDINGS OF THE SECTION OF GEOLOGY

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## OFFICERS :

*Chairman :* Dr. C. Anderson.

*Hon. Secretaries :* Dr. G. D. Osborne and Mr. R. O. Chalmers, A.S.T.C.

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Nine meetings were held during the year, the average attendance being ten members and nine visitors. The above officers were elected for the year 1936.

March 25th.—Mr. E. A. Rudd, M.Sc., of Oil Search Ltd., gave an address on "Personal Impressions of Economic Geology in America".

April 17th.—Exhibits : (1) By Dr. Anderson : Jawbone of *Nototherium* from the Watut River, Mandated Territory, New Guinea. (2) By Mr. Naylor : *Favosites* in coarse tuff from Goulburn, N.S.W., probably Silurian.

Professor W. R. Browne addressed the Section on "Some suggestions regarding Cambrian and Ordovician Palaeogeography of Australia".

May 15th.—Professor Macdonald Holmes addressed the Section on "Soil Erosion".

June 19th.—An address was given by Miss F. M. Quodling on "Some experiments in crystallisation, with special reference to some correlations with igneous rock textures".

July 17th.—Exhibits : (1) By Mr. Waterhouse : (a) "Ventzu-Shih" (literally Swallow Stone) from Drepanura Limestone, of Middle Cambrian age, Wen R., China. Contains *Drepanura premesnili* and *Agnostus chinensis*. (b) Banded shales from Mt. Isa showing in some cases replacement by sulphides. Some showed carbonaceous bands. (2) By Dr. Ida Brown : (a) *Aphrophyllum* sp. from Taree, N.S.W. (b) *Lithostrotion stanwellense* Eth. fil. from Taree, N.S.W. (c) An exhibit of cellulose "peels" illustrating the study of structures in sections of corals. Details of the method of preparing given. (3) By Miss F. M. Quodling : (a) Piece of cellophane showing a biaxial interference figure. (b) Cellophane which is birefringent folded to show orders of interference colours dependent on successive thicknesses of the material. (4) By the Australian Museum : (a) Antimony from Ashford, N.S.W. (b) Pyromorphite from Mt. Isa, Queensland. (c) Aragonite with a trace of strontium from Prospect. (d) Topaz from Nigeria, with specimens from Oban, N.S.W., for comparison. (e) Dreikanter (large collection from Paten, near Wanganui, N.Z.).

August 21st.—Mr. J. A. Steers, Lecturer in Geography, University of Cambridge, delivered an address on "East Anglian Coasts", illustrated by many maps. This meeting was held in conjunction with the Geographical Society.

September 18th.—An address on the "Geomorphology of Eastern Queensland" was delivered by Mr. C. A. Sussemilch.

October 16th.—Rev. Dr. R. T. Wade gave an address on the Falkland Islands.

November 20th.—Mr. E. C. Andrews gave an address illustrated by lantern slides on "Norway, Spitsbergen and Iceland". He also gave an outline of Caledonian and Hercynian movements in Europe and Spitsbergen.

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ABSTRACT OF PROCEEDINGS  
OF THE SECTION OF  
**PHYSICAL SCIENCE**

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OFFICERS :

*Chairman* : W. H. Love, B.Sc., Ph.D.

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G. H. Briggs, J. P. Madsen, Major E. H. Booth,  
Messrs. G. W. C. Hirst, and G. H. Godfrey.

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Eight meetings were held during 1936.

April 29th.—Messrs. R. G. Giovanelli and D. Akehurst : “ Experiences at the Commonwealth Solar Observatory.”

June 17th.—Miss D. Stephen, B.Sc. : “ Photo-chemical Decomposition.”

July 8th.—Dr. W. G. Baker : “ The Propagation of Waves Normally to a Stratified Medium.”

July 22nd.—Mr. Kel. J. Vaughan : “ Sound Motion Pictures.”

August 5th.—Mr. K. R. M. Hart, B.Sc., M.E. : “ Applications of Motion Cinematography to Research.”

September 23rd.—Professor V. A. Bailey : (i) “ Some Developments of the Theory of Radio Interaction.” (ii) A new type of electrometer was demonstrated.

October 21st.—Mr. J. M. Somerville, B.Sc., B.A. : “ The Behaviour of High Energy Particles in the Earth's Magnetic Field.”

November 4th.—Mr. D. M. Myers, B.E., B.Sc. : “ The Differential Analyser—a Machine for Solving Differential Equations.”

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